NITROUS OXIDE EMISSIONS UNDER DIFFERENT CORN FIELD MANAGEMENTS IN THE UNITED STATES

BY

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THESIS

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Abstract

Nitrous oxide (N_2O) is a potent greenhouse gas that also contributes to stratospheric ozone depletion. Intensive nitrogen fertilizer use has increased agricultural N_2O emissions and motivated research efforts to identify field management techniques that best mitigate N_2O emissions and reduce these negative environmental impacts.

In this study, field N_2O emissions were quantified during the 2016 growing season by direct field measurement from corn fields in Champaign, Illinois. Measurements were used to compare N_2O emissions between plots differing in fertilizer rate, cover cropping, and tillage. In addition, corn fields in Illinois, Minnesota, and Colorado were modeled using the process-based Denitrification Decomposition (DNDC) model, which is used to predict trace gas emissions from agriculture based on field and climate conditions. The DNDC model was evaluated for predicting N_2O emissions from corn cropping systems in the United States by comparing published field measured emissions to model predictions.

Field N_2O emissions from the Illinois site were generally low (0-211 gN/ha/d), making observed differences between treatments difficult to discern. While fertilized plots had up to 93% higher N_2O emissions than unfertilized plots on some days, the difference was not significant in most cases ($P>0.05$). Cover cropping and tillage treatments did not significantly affect N_2O emissions.

Model results from DNDC did not consistently predict magnitudes and trends of N_2O emissions at the daily scale, especially during years of heavy rainfall after drought. DNDC predictions consistently included high N_2O emission peaks before fertilization in late winter to early spring. However, such peaks were not observed in the Colorado field measurement study, the only one that included year-round weekly measurements. Cumulative growing season modeled and measured N_2O emissions were of similar magnitude, although their difference was statistically significant for the Colorado site ($P=0.0009$). DNDC results accurately reflected cumulative emission trends associated with varying fertilizer rate, but not those from tillage differences, likely because the influence of tillage on N_2O emissions is not well parameterized in the model due to lack of consensus on tillage effect. Model calibration did not improve N_2O emission predictions beyond the year and treatment it was calibrated for. DNDC is useful for predicting cumulative growing season N_2O emission trends associated with fertilizer application, but needs further modification to improve daily scale predictions and trends associated with other managements.

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1. Introduction

The nitrogen cycle is the movement and transformation of nitrogen species between the atmosphere, geosphere, hydrosphere, and biosphere. Managing the nitrogen cycle is so important that it has been identified as one of the fourteen grand challenges for engineering today [1]. We need to understand and manage the nitrogen cycle because anthropogenic activities have dramatically influenced the natural balance leading to many negative externalities, including global climate change, ozone depletion, eutrophication, loss of biodiversity, and air quality concerns [2]. Promoting sustainable human-environment interactions will minimize these negative environmental and human health impacts.

Nitrogen (N) is necessary for all life, and although N is the most abundant element in the atmosphere as inert dinitrogen gas (N_2), N_2 is not readily available for incorporation into living cells. The strong triple bond of N_2 needs to be broken before the N can be converted into a usable form. Before humans began influencing the nitrogen cycle, N_2 bonds were broken through two natural processes: lightning fixation and biological nitrogen fixation. Biological nitrogen fixation occurs when nitrogen-fixing bacteria convert N_2 into ammonia (NH_3) or ammonium (NH_4^+). Some nitrogen-fixing bacteria maintain a symbiotic relationship with legume plants, such as soybeans.

Once N_2 has been converted to NH_4^+, it can be further transformed through biological uptake or nitrification. Plants that can use NH_4^+ as their nitrogen source will consume NH_4^+ and convert it into organic N in the form of DNA, RNA, or proteins, necessary to promote growth and sustain life. Plants then transfer the organic N to animals that consume them or decomposers that mineralize organic N back into NH_4^+. Soil NH_4^+ is also transformed through nitrification, an aerobic process (requires oxygen) that transforms NH_3 or NH_4^+ into nitrate (NO_3^-) (Figure 1). The first series of steps in nitrification are catalyzed by ammonia-oxidizing bacteria and ammonia-oxidizing archaea. The final step of nitrification is catalyzed by nitrite-oxidizing bacteria.

$$NH_3 \; or \; NH_4^+ \rightarrow H_2NOH \rightarrow N_2O + NO \rightarrow NOH \rightarrow NO_2^- \rightarrow NO_3^-$$

Figure 1. Overview of the nitrification, an aerobic process common in agricultural soils.

Soil NO_3^- can then be incorporated into plants through biological uptake or be further transformed by denitrification. Denitrification is an anaerobic process (no oxygen) that uses organic carbon (C) and transforms NO_3^- into N_2 (Figure 2). This multi-step process does not always reach completion before intermediate gases escape into the atmosphere. Nitric oxide (NO) and

N_2O gases both participate in ozone depletion, NO is extremely hazardous and contributes to acid rain, and N_2O is a potent greenhouse gas [2-4]. While the intermediate gases pose several negative human and environmental impacts, N_2 is inert. Denitrification is considered incomplete when the intermediate gases escape before being fully reduced to N_2.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Figure 2. Overview of denitrification, an anaerobic process common in agricultural soils.

Human activities interfere with the natural balance of the nitrogen cycle by increasing the amount of reactive nitrogen in the environment faster than it can be returned to its inert state. Humans create reactive nitrogen by burning fossil fuels, cultivating more legumes, and using the Haber-Bosch process to generate synthetic fertilizers [2]. Agriculture contributes to all three of these areas, as fossil fuels are burned during field management and in the Haber-Bosch process and fertilizers and cultivation of legumes increase available soil N for crops. Considering fertilizer application alone, it is estimated that only half of fertilizer is taken up by crops, while the other half is lost to the hydrosphere as NO_3^- or to the atmosphere as NH_3, NO, N_2O, or N_2 [2]. Overall, direct emissions from agricultural soil are the largest source of N_2O in the United States [5]. These N_2O emissions contribute significantly to global climate change, as N_2O has 300 times more global warming potential than carbon dioxide (CO_2) over 100 years [5].

Once reactive nitrogen enters the nitrogen cycle, it is rapidly transformed and transferred through the atmosphere, hydrosphere, geosphere, and biosphere, with the potential to cause negative environmental and human health effects at each step. This sequence, known as the nitrogen cascade, is why it is important to minimize the amount of reactive nitrogen that is formed and to ensure that all reactive nitrogen is used efficiently for its intended purpose [2]. Therefore, research aims to identify field managements that increase crop N uptake and reduce N emissions.

One way to identify nutrient management practices that promote N uptake efficiency is to quantify N emissions from agriculture and compare them across managements. There are two ways to quantify these N emissions: direct field measurements and model predictions. Both methods are commonly used and each has limitations. Field measurements are considered the most accurate, but are time intensive and sometimes costly. Modeling approaches can save time and money, but potentially at the expense of accuracy. Choosing an appropriate approach to quantifying N emissions is important for assessing the impact of field management techniques on N emissions.

In the past, extensive effort has been aimed at reducing NO_3^- emissions from agriculture, as NO_3^- losses to the hydrosphere contribute to eutrophication, hypoxia, loss of biodiversity, and habitat degradation [2]. With growing concern about global climate change and better understanding of the nitrogen cascade issues, more efforts have been aimed at gaseous nitrogen emissions from agriculture. N_2O emissions and their differences across agricultural field managements have varied across studies, as reviewed in Section 2.2. Therefore, further research efforts are needed to identify agricultural field management strategies that reduce N_2O emissions and to determine the best approach to quantifying N_2O emissions from agriculture.

The aims of this study were to (1) compare measured N_2O emissions between corn fields under different fertilizer, tillage, and cover cropping management in Illinois, (2) model N_2O emissions using DNDC for sites under different fertilizer, tillage, and cover cropping management in the United States, and (3) evaluate DNDC by comparing modeled N_2O emissions with field measurements.

2. Literature Review

To give proper context to the methods described in this thesis, the literature review will discuss current trace gas measurement methods and agricultural N_2O measurement and modeling studies. Of several trace gas sampling methods, static chambers were the best option for this study because they are simple, cost-effective, portable, commonly used in other studies, and appropriate to compare the effects of different treatments on N_2O emissions. Based on my literature review of agricultural N_2O emission measurement studies in the United States, the influence of tillage, cover cropping, and their interaction effects with fertilizer were identified as areas with incomplete understanding or lack of consensus. Considering the different modeling approaches to estimating N_2O from agricultural systems, process-based modeling was identified as the most accurate, versatile, and robust option, but it still requires model evaluation and calibration. The field campaign and model evaluation study described in this thesis were developed to address the identified research gaps in agricultural N_2O measurement and further evaluate process-based models for agroecosystems in the United States.

2.1 Trace gas measurement methods

Before beginning chamber construction and field measurements, I conducted a literature review to identify which sampling method would be appropriate for my study. Current methods for measuring trace gas emissions include eddy covariance, eddy accumulation, flux-gradient methods, and chambers. Eddy covariance, eddy accumulation, and flux-gradient methods are used for large landscapes with homogenous surface sources, while chambers are the suitable method for small plots and small gas fluxes. In this section, each method will be summarized and assessed based on strengths and limitations outlined in the literature [6-9].

Micrometeorological approaches, including eddy covariance, eddy accumulation, and flux-gradient methods, are influenced by atmospheric stability, which controls transport and mixing of gases in the atmosphere. Eddy covariance methods give an instantaneous measure of vertical flux as the product of wind speed and concentration measured by high sensitivity instruments. Eddy accumulation collects and stores samples in up and down sampling bins based on vertical wind direction, which are analyzed and used to calculate gas flux as functions of wind speeds and concentrations in both directions. Flux-gradient methods calculate vertical gas flux based on a concentration gradient and eddy diffusivity constant.

Micrometeorological approaches can provide accurate flux estimations for a specific site. As part of their setup, they measure other meteorological parameters at the site which can be directly compared with flux data to identify correlations. However, these approaches require electrical power to collect samples and monitor meteorological parameters. Therefore, areas without electricity cannot effectively use these methods without batteries, solar panels, or other forms of portable power. In addition, they may require rapid response equipment, which in some cases are not feasible for long-term field campaigns. Micrometeorological methods are also only appropriate for large areas with uniform soil; they are not feasible for small plots with different treatments in the same field.

When micrometeorological methods are not feasible, chambers may be appropriate. Chambers can be grouped by type: open or closed, static or dynamic. Open chambers have continuous air flow and compare the concentration of the gas found outside the chamber to that found inside the chamber air stream. Flux is calculated under this method by multiplying the concentration difference by volumetric flow rate and the inverse of chamber surface area. Conversely, closed chambers are sealed to prevent air flow, except when a vent is used to control pressure gradients. Air is sampled from the chamber at time intervals to determine the change in gas concentration with time. Flux is the product of concentration rate of change, chamber surface area, and inverse chamber volume. Closed chambers are simpler and have a larger detection range. Closed chambers can be static or dynamic. Static chambers involve gas sampling in the field and subsequent laboratory analysis. Dynamic chambers require power and often automatically direct air from the chamber to an in-field gas analyzer.

Dynamic chambers simplify field sampling once installed and allow for immediate results when in-field gas analyzers are employed. Yet, static chambers are often the preferred method as they are inexpensive, require no power, and are easily implemented and adaptable. A disadvantage of using chambers is that they have a small footprint and need many replicates.

For considering emissions from a small field with different treatments within the same area, it is not possible to apply micrometeorological approaches. In addition, the fields used in this study do not have electrical power, making static chamber the most feasible and economical method. The portability and ability to construct many chambers at low cost enables the method to be used on different fields at the same time, allowing for more treatment comparisons. Static chamber methods have also been used in 95% of all published N_2O studies [8], so this method also

allows for the most direct comparison of results. For these reasons, static chambers were identified as the most feasible, cost-effective option for my study, allowing consideration of multiple different treatments simultaneously in small plots.

2.2 Agricultural N_2O measurement studies

Since the negative environmental consequences of intensive fertilizer management have been identified, research efforts have been aimed at minimizing negative environmental consequences associated with food production [10]. Approaches have included fertilizer management, reduced tillage, diversified crop rotations, controlled irrigation and drainage, and treatment systems [11-14]. As the research described in this thesis is focused on management efforts to reduce N_2O emissions from corn fields in Illinois, the literature review was focused on similar studies and is summarized in Table 1. Specifically, the search included chamber-based field studies in the United States that experimentally investigated any of the following managements: fertilizer rates, fertilizer type, tillage type, crop rotations, cover cropping, irrigation, and drainage.

Table 1. Agricultural N_2O measurement studies summary

Location	Managements	Effect	Max flux (gN/ha/d)	Ref
Colorado	N type	enhanced efficiency < urea	39.5	[15]
Minnesota	tillage N type	none none	47.5	[16]
Colorado	tillage crop rotation N rate	none none linear increase with N rate	73.6	[17]
Ohio	tillage	no till < chisel plow	90 *	[18]
Colorado	tillage N rate	effect differed by year linear increase with N rate	132	[19]
Iowa	CC N rate	none non-linear increase with N rate	350 *	[20]
Minnesota	Tillage N type	effect varied with N type urea & UAN < AA	360 *	[21]
Michigan	Irrigation	increase with N + water	397	[22]
Iowa	Tillage CC	none none	400 *	[23]
Illinois	N type	polymer-coated urea < urea & AA	1,086	[24]
Midwest	tillage N rate N type	none none none	3.73 **	[25]

** maximum flux estimated from figure in paper; ** mean flux reported instead of maximum flux*
AA = anhydrous ammonia; CC = cover crop; N = nitrogen; UAN = urea ammonium nitrate

Fertilizer management has been the primary focus of most research efforts as its effects are immediate and often significant [2, 26, 27]. It is expected that N_2O emissions will increase with increasing substrate concentrations for nitrification and denitrification (NH_4^+ and NO_3^-, respectively). Studies comparing fields under different fertilizer rates found that fertilizer increased emissions in almost all cases. However, they have differed in conclusion about the relationship between fertilizer rate and N_2O flux, with some identifying a linear relationship [17, 19, 27] and others an exponential one [11, 20, 28, 29]. Studies that identify an exponential increase in N_2O emissions with N rate attribute it to exceeding the N needs of the crops and therefore increasing N losses. Studies have also compared N_2O emissions from different fertilizer types. Manure was shown to increase N_2O emissions relative to synthetic fertilizers [11]. Comparing synthetic fertilizers, urea decreased emissions relative to NO_3^--containing fertilizers and anhydrous ammonia [11, 21]. Enhanced efficiency synthetic fertilizers sometimes reduced N_2O emissions relative to conventional fertilizers [11, 24], but were also found in some studies to have no significant impact [16]. In addition, studies considering the effect of N timing and locations are extremely limited and show inconclusive results [11]. Future research is still needed to determine interactive effects between N management and other field management techniques.

Since reduced tillage practices increase soil organic carbon (SOC) and decrease CO_2 emissions [25, 30-32], subsequent studies have investigated the influence of tillage on N_2O emissions. However, conflicting results have been obtained. Decreased tillage is expected to increase N_2O emissions by reducing drainage, leading to more anaerobic zones and increased denitrification. Several studies have found increased N_2O emissions with decreased tillage [33-36], while another observed the opposite relationship [18]. Many studies found tillage to have no significant effect on N_2O emissions [11, 12, 16, 23, 25]. The differences between studies have been attributed to the time since different tillage was established, site-specific conditions, or interaction effects with other treatments [11, 12]. Yet, studies comparing tillage within one field site found that tillage sometimes had no effect and sometimes increased or decreased N_2O emissions [17, 19, 21, 37]. The influence of tillage on N_2O emissions is still an area that needs further research.

Few studies have considered the influence of different crop rotations or cover cropping on N_2O emissions. One study found that fields under corn-soybean rotation have higher emissions during corn years than fields under continuous corn cultivation [19], but a similar study found that

corn emissions were similar regardless of the previous year's crop [35]. A lab study found that cover cropping has the potential to reduce N_2O emissions, but was unable to reproduce these results in the field [20]. Another field study also found no significant difference in emissions between fields using rye cover crop and those without [23]. Cover cropping may increase N_2O emissions by increasing C availability for denitrification. Alternatively, cover cropping may decrease N_2O emissions by decreasing N availability for denitrification by direct crop uptake. It is likely that the effect of cover cropping varies throughout the season as the cover crop grows and dies. The limited number of studies and understanding of the influence of crops on N_2O emissions warrants further study.

The influence of precipitation, irrigation, and drainage on N_2O emissions has been considered in a few field studies. N_2O emissions increase after major precipitation events and there is a strong positive correlation between N_2O flux and water filled pore space [16, 35, 38, 39]. This relationship is expected because precipitation increases soil water content and anaerobic zones, which increases denitrification. Similar observations were found in controlled irrigation studies, although they also identified an important connection between fertilizer and precipitation [40]. When irrigation occurred much later than fertilization, N_2O emissions decreased with the tradeoff of increased NH_3 volatilization [40]. Similarly, a separate irrigation study found that N_2O emissions were not only dependent on water but also N and C availability [22]. One study considered the influence of drainage and found that drained soils showed lower N_2O emissions relative to undrained ones [18]. Drained soils should have lower N_2O emissions because draining increases aeration and decreases water logging, leading to decreased denitrification. While the influence of precipitation, irrigation, and drainage appear significant, additional studies and consideration of their interaction effect with nutrient availability is necessary to fully understand these relationships.

Based on these identified research gaps, the influence of tillage and cover cropping on N_2O emissions were considered in the field campaign described in this thesis. In addition, the interaction effects of these managements with fertilizer rate were considered.

2.3 Agricultural N_2O modeling approaches

Models have been developed to predict N_2O emissions at local, regional, and global scales, and vary in goal, complexity, and accuracy. Therefore, it is important to select the model most

appropriate for a given goal and to evaluate the model to ensure it is well suited. In some instances, model calibration may also be necessary to improve overall model performance. To ensure that an appropriate model was selected for this study, I conducted a literature review on current N_2O modeling approaches and best practices.

The most common methods used to predict N_2O emissions are described by the Intergovernmental Panel on Climate Change (IPCC) and include three tiers that increase in complexity [27]. Tier 1 is a simple linear equation multiplying nitrogen inputs of a given area by empirically derived emission factors. The default emission factor is 1% for any N applied to or mineralized in agricultural soil [27]. However, this emission factor was determined based on only a few studies and has large uncertainty (0.003-0.03) [27]. Tier 2 is a more detailed version that is appropriate when country or site specific activity data and emission factors are known. Tiers 1 and 2 are typically used to estimate national or global N_2O emissions rather than emissions for a specific site or management. Tier 3, direct field measurements or process-based modeling, is considered to be more accurate, but requires significantly more effort and financial resources than the other two tiers. In this study, a Tier 3 approach was used.

The two most common process-based models used to predict N_2O emissions from agricultural soils are the DNDC model [41, 42] and daily CENTURY (DayCent) [43]. Both models simulate soil climate, crop growth, decomposition, and nitrogen mineralization and transformations. However, the models were originally developed with different purposes and have since been adapted in different ways which ultimately affects their prediction potential under different scenarios. DNDC was developed for nitrogen biogeochemical cycling in agroecosystems, while DayCent originally focused on grassland soil biogeochemistry. Both models were designed for simulations at the site level, but DNDC expanded the model to include a regional mode. DNDC includes a more detailed denitrification submodel that is based on microbial growth kinetics in the step-wise reduction pathway. Additionally, DNDC simulates more N loss pathways, including NH_3 volatilization. DNDC was chosen for this study because it was developed specifically for agricultural ecosystems, considers microbial growth kinetics, was used successfully during previous studies at the University of Illinois [44], and offers more options, such as wetland modeling, which will be helpful in future facets of the research project.

DNDC model inputs are ecological drivers including climate parameters, soil physical properties, vegetation, and anthropogenic activity (Figure 3) [42]. The ecological drivers are used

in the soil climate, crop growth, and decomposition sub-models to calculate soil environmental variables for each day [42]. The soil environmental variables, including soil temperature, moisture, pH, Eh, and substrate concentrations, are incorporated into the denitrification, nitrification, and fermentation sub-models to calculate model outputs at the daily timescale [42]. While the model was originally developed to predict N_2O, CO_2, and N_2 emissions, it was later expanded to include methane (CH_4) and NH_3 [45].

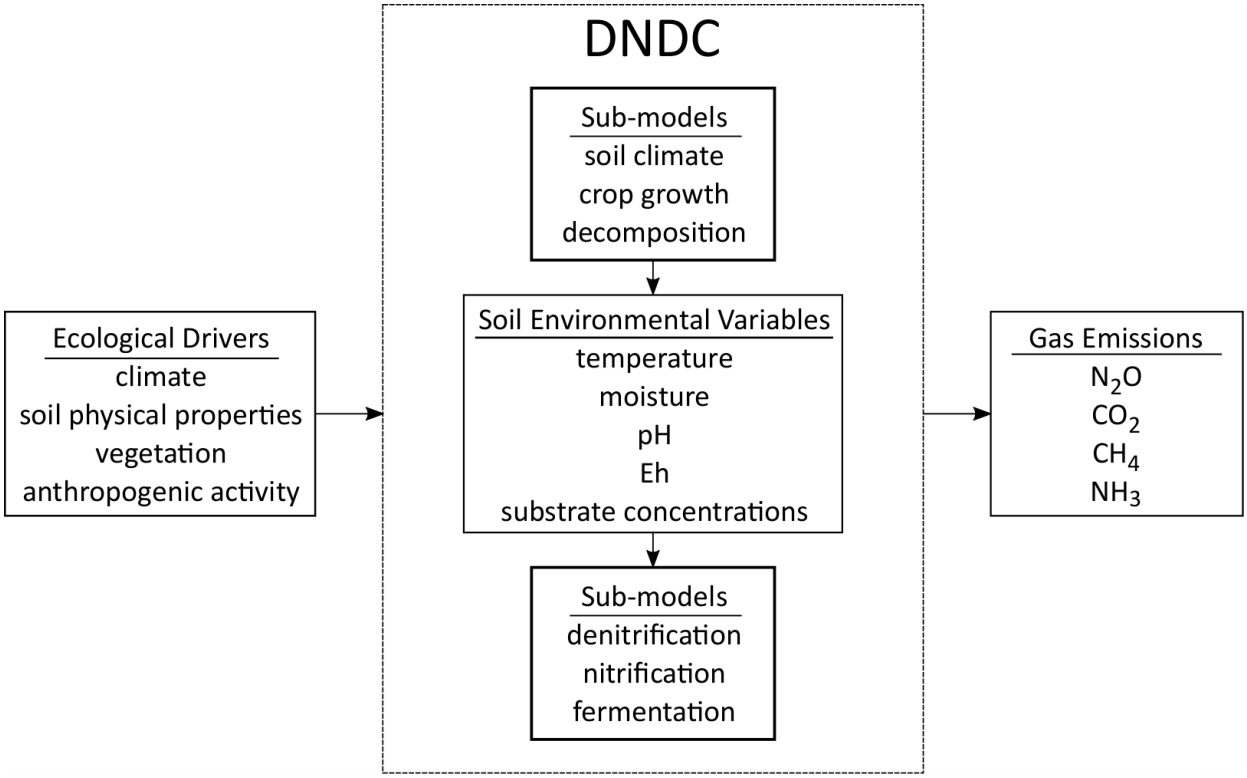

Figure 3. Simplified conceptual model of DNDC including model inputs (ecological drivers), DNDC sub-models and intermediate variables, and select model outputs (gas emissions). Adapted from Li 2000 [42].

In DNDC, N_2O production is based on the contributions from nitrification and denitrification. The concept of the anaerobic balloon is used in DNDC when allocating substrate to the nitrification and denitrification sub-models [42]. The anaerobic balloon, which is controlled by redox potential, swells at low Eh (250-350 mV) and shrinks at high Eh (250-700 mV). In the lower Eh range, denitrification dominates and more substrate is allocated to the denitrification sub-model [42]. Likewise, higher Eh ranges indicate higher concentrations of O_2, which is used as the electron acceptor in nitrification until other reduction pathways become more favorable [42]. In addition to substrate concentrations, other soil factors control denitrification and nitrification in DNDC. Production of N_2O through nitrification is influenced by soil temperature, moisture, pH,

dissolved organic carbon (DOC) concentration, and NH_4^+ concentration [42]. Production of N_2O through denitrification is influenced by soil temperature, moisture, pH, Eh, and substrate concentrations (DOC, NO_3^-, NO_2^-, NO, N_2O) [42].

DNDC studies have been conducted for agricultural sites within the United States, Canada, Ireland, Germany, and China, among others. Several agricultural systems have been modeled including grasslands, wheat, bean, corn, soybean, and rice paddy. Model evaluation studies similar to that described in this thesis are summarized in Table 2. Some studies have only considered the default model [46], while others have used systematic model calibrations to improve model predictions for their sites [47-51]. While many studies focused primarily on DNDC model evaluation, some compared its performance to other models like DayCent [46, 47].

Table 2. Agricultural N_2O modeling studies summary

Country	Management	Calibration	Spin-up time	DNDC performance	Ref
Ireland	pasture	no	NR	Overpredicts, high Feb peak	[46]
Canada	bean/wheat, till vs. reduced till	parameter optimization	10 years	Sometimes overestimates, sometimes underestimates	[48]
Canada	corn/soy/wheat, ± tillage, ± fertilizer	parameter optimization	18 years	Suitable for long term estimates (5+ years)	[51]
Ireland	pasture	parameter optimization	NR	Reasonable accuracy after calibration for annual emissions	[49]
USA	corn, ± tillage, fertilizer type	ML parameter optimization	none	Reasonable accuracy after calibration for annual emissions	[52]
Canada	corn/soy/wheat, ± tillage, ± fertilizer	ML parameter optimization	2000 years	Reasonable accuracy after calibration for annual emissions	[50]
Canada	wheat, ± fertilizer	ML parameter optimization	10 years	Captures difference between fertilized and unfertilized	[47]
Germany	bean/wheat, till vs. reduced till	ML parameter optimization	NR	Sometimes overestimates, sometimes underestimates	[37]

ML – multi-level; NR – not reported

DNDC evaluation studies and review articles have highlighted several suggestions when using DNDC to model N_2O emissions. Since temperature and precipitation are key drivers in DNDC for the microbial pathways that produce N_2O emissions, it is advised to run multi-year simulations in order to capture variability between years from climate [53]. Studies recommend site-specific model calibrations to improve model predictions [37, 49]. While many studies do not explicitly state the need for calibration, it is apparent that DNDC calibration is necessary, as they only report results after calibration [47-52]. Most studies recommend running several years of

spin-up time to ensure soil C and N pools stabilize before the years of interest. The years of spin-up used have varied from 0 [52] to 2000 years [50], with 10 years the most often used and recommended [47, 48].

DNDC model evaluation studies have reached various conclusions when comparing modeled and measured N_2O emissions. Most studies found that DNDC was incapable of accurately predicting emissions at the daily scale [37, 48], although one study found that after calibration DNDC predicted similar peaks in N_2O emissions at the daily scale [52]. It was more common for studies to find that DNDC can predict annual magnitudes and trends of N_2O emissions after calibration [48-50, 52]. One study found that DNDC was only able to capture the difference between fertilized and unfertilized plots, while other managements were not well simulated [47]. In some cases, DNDC severely overpredicted emissions [46]. Others found no consistent trend with predictions, as N_2O fluxes sometimes were overestimated and other times underestimated [37, 48].

Based on this literature review, DNDC needs site-specific model calibrations in most cases. In addition, while it can capture the influence of fertilizer on agricultural N_2O emissions, it may require further modification to improve its predictions of the impact of other management practices. Thus, this study compares default and calibrated DNDC versions after 10 years of spin-up time for three corn-cropping sites with different climate and soil properties but similar field managements.

3. Methods

3.1 Field measurements

3.1.1 Study sites

Two corn-soybean fields with identical climate and soil properties but different field managements were chosen to study the influence of different field management techniques on N_2O emissions. The Precision Zonal Management (PZM) and Lo Farm field sites (Figure 4), part of the Crop Sciences Research and Education Center (CSREC), are located south of the University of Illinois in Champaign, Illinois (40.049018N, 88.236105W and 40.042407N, 88.224068W, respectively). The soil is predominantly classified as Drummer silty clay loam (fine-silty, mixed, superactive, mesic Typic Endoaquoll) with average pH 6.7, bulk density 1.33 g cm^{-3}, and SOC 48 g kg^{-1} [54]. Mean annual precipitation and temperature based on the 1981-2010 Climate Normals are 100.8 cm and 10.5°C, respectively [55].

Figure 4. Locations of Lo Farm and PZM fields. Both fields are east of 1st Street near the intersection with Old Church Road in Champaign, Illinois, south of the University of Illinois. Source: Google maps [56]

The corn-soybean rotation field at PZM was established in 2011 using randomized complete block design with four blocks. Prior to this, the field was under typical corn-soybean rotation and conventional tillage management. Within each block, the two main treatments, tillage and cover cropping, were considered at two levels each. Tillage treatment levels included (i) chisel plow and (ii) ridge till. Cover cropping treatment levels were (i) no cover cropping and (ii) rye cover cropping planted in late October and killed by herbicide in mid-April each year. Fertilizer treatments were broadcast applied to corn plots as urea ammonium nitrate (UAN) 28% at a rate of 180 kg N ha^{-1}. Additionally, unfertilized subplots were established within each of the different plots. For this study, a total of four different treatment combinations under corn and chisel plow were considered in blocks 1-3: cover cropping + fertilizer, cover cropping control (no fertilizer), fertilizer, and control (no fertilizer). In 2016, corn was planted April 23 and harvested October 3.

The corn-soybean rotation field at the Lo Farm was converted from historical conventional tillage to no tillage in 2007. Fertilizer treatments were broadcast applied to corn plots as UAN 28% at a rate of 202 kg N ha^{-1}. In 2016, fertilizer was applied May 16, and corn was planted May 26 and harvested in early October.

3.1.2 Gas sampling and analysis

Gas samples were collected using the static chamber method and analyzed by gas chromatography. Resulting concentrations were used to obtain fluxes by linear regression. These methods were chosen based on literature recommendations and feasibility (Section 2.1) [7, 8]. This section outlines specific details of the methods used in this field study.

Chambers bases and tops (Figure 5) were constructed out of 12” diameter polyvinyl chloride (PVC) pipe, which is inert to N_2O. Each chamber base was 15 cm tall with one edge beveled 45° to facilitate installation in the soil. Each chamber top consisted of a 10 cm tall ring with a ¼” thick PVC sheet cut and cemented to one edge. The entire chamber top was covered with silver Mylar tape to reflect solar radiation and prevent temperature gradients. A 15 cm long ¼” diameter stainless steel tubing was fitted into one side of the chamber top as a vent. To prevent dilution when using the vent, it was placed close to the surface, pointed away from the dominant wind direction. Tractor tubing and rubber weather seal were used to create an airtight seal between the chamber top and bottom during field sampling. A ½” hole in the chamber top and 20 mm butyl

rubber stopper made the sampling port. See Appendix A: Chamber Construction for a detailed list of materials and step-by-step construction methods.

Gas sampling protocols were developed based on literature recommendations and are summarized here [6-8, 57]. For stepwise procedure, a list of materials, and further details, see Appendix B: N2O Sampling Protocol. To prevent soil disturbance from influencing results, chamber bases were installed at least 24 hours prior to the first sampling time and remained in the field unless field operations required removal. To account for temporal variability, chambers should be sampled during the time period that corresponds to average daily N_2O flux. In the absence of such information, sampling occurred during a time period of average daily temperature (8am-12pm) on all sampling dates. Ideally, sampling should occur once per week during low N_2O flux time periods and more frequently when high N_2O flux is expected. However, in 2016, it was only feasible to sample each site seven times between the dates of planting and harvesting Table 3. All sampling supplies, including syringes, needles, vials, and septa, were clean and non-reactive to N_2O. No more than 48 hours prior to sampling, 10 mL clear glass vials (Fisher Scientific, Hampton, NH) with 20 mm Pharma-fix PTFE gray butyl rubber septa (SUN SRi, Rockwood, TN) were crimped with 20 mm standard aluminum seals (SUN SRi, Rockwood, TN) and evacuated for at least 90 seconds using a vacuum pump at 26.5 in Hg pressure. Each chamber was sampled four times within one hour: at 0, 20, 40, and 60 minutes from the time of chamber top placement. At each time point, a 15 mL gas sample was taken from the chamber and injected at overpressure into an evacuated glass vial using a 20 mL disposable syringe (Becton Dickinson and Company, Franklin Lakes, NJ) and 23 gauge needle (Becton Dickinson and Company, Franklin Lakes, NJ). Samples were only accepted if the vial seal held during injection. Rejected samples were immediately resampled and injected into a backup evacuated vial. Vials filled with gas samples were stored in a shock-resistant carrying case until analysis. All samples except those taken on 4/28 and 5/30 were analyzed within 24 hours of sampling to minimize gas losses. For those two dates, samples were stored at room temperature and analyzed on 6/2.

Table 3. Field management and sampling dates at the PZM and Lo Farm field sites in Champaign, IL, in 2016.

	PZM	Lo Farm
Fertilization date	4/23	5/16
Tillage date	10/13	-
Planting date	4/23	5/26
Sampling dates	4/26, 4/28, 6/8, 6/23, 7/7, 7/21, 8/3	5/30, 6/1, 6/8, 6/23, 7/7, 7/21, 8/3
Harvest date	Early October (9/28-10/7)	10/3

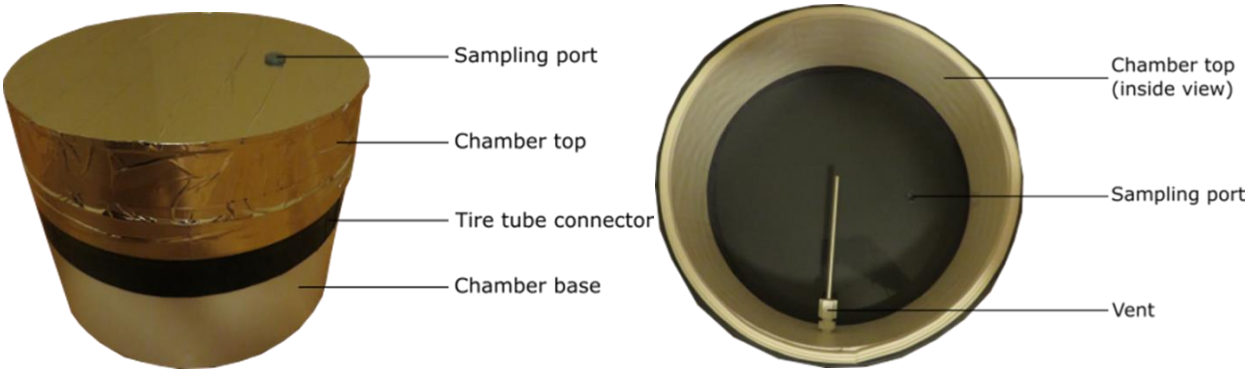

Figure 5. (Left) Side view of static gas chamber top and base used in field gas sampling. (Right) Inside view of static gas chamber top.

At the PZM site, one chamber was placed in row with the corn for each of three replicate plots per treatment (Figure 6). All plots sampled at the PZM site were planted to corn and used chisel plow tillage. Four treatments with three replicates of each were studied within these plots: cover cropping with fertilizer, cover cropping without fertilizer, fertilized only, and unfertilized only. At the Lo Farm site, two chambers were placed (one in row with the corn and one between rows) for each studied plot. Two treatments with three replicates of each were studied at the Lo Farm: in row with corn and between rows. Both treatments were under the same management: corn year of corn-soybean rotation, fertilized, no tillage, and no cover cropping.

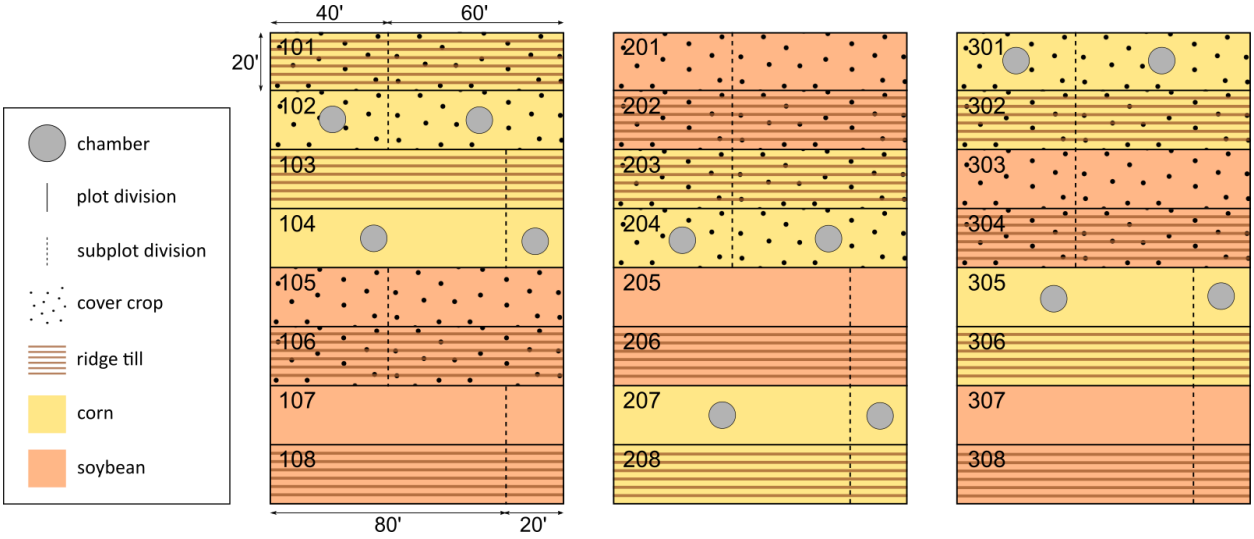

Figure 6. PZM block setup for 2016 field campaign. Plots were labeled by block and plot within each block, where the first number indicates the block and the last number indicates the plot. Chamber locations are approximated and are not to scale. Plots without dots were under no cover cropping management. Plots were under chisel plow management unless marked with horizontal bars for ridge till. Within each plot, the smaller subplot was unfertilized and the larger portion received 28% UAN fertilizer.

Gas samples were analyzed for N_2O concentration using a gas chromatograph equipped with electron capture detector and auto sampler (Shimadzu GC-2014 and AOC 5000 Plus, Kyoto, Japan). Helium (Airgas, Radnor, PA) was used as the carrier gas and a combination of 100 ppm N_2O (Airgas, Radnor, PA) and helium were used to create N_2O standards of 0, 0.1, 0.66, 0.99, 1.64, 3.33, and 6.67 ppm (μL N_2O/L air). Based on recommendations, samples were run in sequence for individual chambers and standards were tested periodically to test for instrument drift. There were no analytical replicates of samples as replicate field plots were used instead.

The two recommended approaches to calculating gas flux are linear regression and non-linear methods. Linear regression was used here to calculate the slope of concentration versus time for each chamber. Flux in μL/m^2/min was calculated as follows:

$$Flux_a = \frac{mV}{A} \quad (1)$$

where m is slope in ppm/min or μL N_2O/L air/min, V is chamber volume in L, and A is chamber soil surface area in m^2.

Flux units were converted to μmol/m^2/min using the ideal gas law:

$$Flux_b = Flux_a \times \frac{P}{RT} \quad (2)$$

where P is atmospheric pressure in atm, R is the gas constant 0.08206 L atm/mol/K, and T is air temperature in K.

Flux units were converted to gN/ha/d using the following conversions:

$$Flux_c = Flux_b \times \frac{mol}{10^6 \mu mol} \times \frac{44\ g\ N_2O}{mol\ N_2O} \times \frac{28\ g\ N_2O - N}{44\ g\ N_2O} \times \frac{60\ min}{hr} \times \frac{24\ h}{d} \times \frac{10^4\ m^2}{ha} \quad (3)$$

3.1.3 Statistical analysis

All statistical analysis was computed in R [58]. The ANOVA assumptions of normality and equality of variance were tested by the Shapiro-Wilk test and the Bartlett test, respectively. In all cases, assumptions were violated, so the Kruskal-Wallis test, a non-parametric alternative, was used to test for variance within the levels of each factor: tillage, cover cropping, fertilizer, chamber location, and date. Significant factors were tested by the Mann-Whitney U test with a Bonferroni correction was used to test levels of significant factors by pairwise comparison. In all cases, a 95% confidence interval was used and significance was found for $P<0.05$.

3.2 Modeling

The DNDC model, outlined in Section 2.3, was used to predict N_2O emissions from field sites in Illinois, Minnesota, and Colorado (Figure 7). Model inputs, including soil parameters (Table 4), climate data (Table 5), vegetation, and human activity, were used to drive submodels and generate model output, including daily N_2O emissions. This section provides relevant model inputs for each field site, model evaluation methods, and model calibration methods.

3.2.1 Modeled field sites

Figure 7. Locations of field sites that were modeled using DNDC. Source: Google maps [56]

Table 4. Soil parameter values used in DNDC model input file development

	Champaign, IL	Rosemount, MN	Fort Collins, CO
Soil texture	Silty clay loam	Silt loam [a]	Clay loam [b]
Bulk density (g cm^{-3})	1.33	1.45	1.36 [b]
Soil pH	6.7	6.5	7.7 [b]
Clay fraction	0.27	0.13	0.31
SOC (kg C $kg\ soil^{-1}$)	0.048	0.028 [a]	0.012 [b]

Sources: a – Venterea et al. 2011 [16]; b – Mosier et al. 2006 [19]; all others – Web Soil Survey [54]

Table 5. Average annual temperatures and precipitation based on the 1981-2010 Climate Normals

	Champaign, IL	Rosemount, MN	Fort Collins, CO
Average temperature (°C)	10.5	6.9	10.1
Average high temperature (°C)	16.3	12.3	17.6
Average low temperature (°C)	4.7	1.4	2.7
Average annual precipitation (cm)	100.8	88.7	40.8

Source: US Climate data [55]

In addition to the N_2O measurements data obtained from the field campaign in Champaign, Illinois (Section 3.1.1), published field data from two corn cropping systems that compared similar field managements were used in model evaluation [16, 19]. For all three sites, a ten year spin-up time was used.

The first field site was in the University of Minnesota's Outreach, Research, and Education Park located in Rosemount, Minnesota (44.75N, 93.06667W). The soil is predominantly classified as Waukegan silt loam (fine-silty, skeletal mixed, superactive, mesic Typic Endoaquoll) [16, 54]. The Minnesota field was established in 1990 using a randomized complete block design with three blocks [16]. Within each block, there were two main treatments: tillage and crop rotation. Tillage treatment levels included (i) conventional tillage (CT) and (ii) no tillage (NT). Crop rotation treatments were not compared in this study as only corn years of corn-soybean rotations were sampled. Additionally, five fertilizer subplots were established within each of the different plots [16]. For my modeling study, only two fertilizer treatments from this study were considered: (i) conventional granular urea (CU) and (ii) no fertilizer control (C) (received starter urea fertilizer at a rate of 4.5 kg N ha^{-1}). Fertilizer treatments were broadcast applied to all plots during corn years at a rate of 146 kg N ha^{-1} [16]. A total of four different treatment combinations (CT-CU, CT-C, NT-CU, and NT-C) were modeled and compared to field measurements.

For model input file development, it was assumed that corn was planted May 9 until 2008, May 5 in 2009, and May 6 in 2010 [16]. Using state estimates, it was estimated that corn was harvested each year on October 20 [59]. Similarly, soybean planting and harvest dates were estimated to be May 25 and October 16, respectively [59]. All other field management data were obtained from site publications [16, 21]. Daily maximum and minimum temperatures, precipitation, wind speed, and humidity data were obtained from the Department of Natural Resources [60] and the Weather Company [61]. Soil physical properties not found within site publications were obtained from the Web Soil Survey [54].

The second field site was in the Agricultural Research Development and Education Center (ARDEC) near Fort Collins, Colorado (40.65N, 104.9833W) [15, 17, 19]. The soil is predominantly classified as Fort Collins loam (fine-loamy, mixed, superactive, mesic Aridic Haplustalfs) [15]. The Colorado field was established in 1999, again using a randomized complete block design with three blocks [19]. Within each block, there were three main treatments: tillage, crop rotation, and fertilizer rate. Tillage treatment levels included (i) conventional tillage (CT) and (ii) no tillage (NT). Crop rotation treatment levels were (i) continuous corn and (ii) corn-soybean rotation. Fertilizer treatments were injected 5 cm below the soil surface as UAN 32% during corn years at a three different treatment levels: (i) 0 kg N ha^{-1}, (ii) 134 kg N ha^{-1} (only for continuous corn treatments), and (iii) high nitrogen, which was 202 kg N ha^{-1} in 2002 and 224 kg N ha^{-1} in 2003 and 2004. For this study, a total of eight different treatment combinations (continuous corn: CT-0N, CT-134N, CT-HN, NT-0N, NT-134N, NT-HN; corn-soybean: NT-0N, NT-HN) were considered with three replicated blocks.

For model input file development, it was estimated that corn was planted April 24 until 2002 and on April 28 beginning in 2003 [19, 59]. Similarly, it was estimated that corn was harvested each year on October 26 [59, 62]. Since soybean planting and harvest dates were unavailable for Colorado, values were estimated based on those found in Nebraska: planting on May 21 and harvest on October 11 each year [59]. All other field management data was obtained from site publications [15, 17, 19]. Daily maximum and minimum temperatures and precipitation data were obtained from the Colorado Climate Center [63]. Soil physical properties not found within site publications were obtained from the Web Soil Survey [54].

3.2.2 Model evaluation

After model runs were completed for each scenario, the DNDC model was evaluated to determine how well DNDC predicts agricultural N_2O emissions. Model evaluation was conducted using three methods: (1) graphical analysis, (2) quantitative analysis, and (3) sensitivity analysis [64]. Graphical analysis allows for visual inspection of the results to determine if the model looks approximately correct. Quantitative analysis then confirms or denies conclusions from visual inspection using statistical techniques. Sensitivity analysis determines how sensitive the model is to changes in given input parameters.

Graphical analysis included plots of N_2O flux versus time, cumulative N_2O emissions, and modeled vs. measured N_2O fluxes. Measured N_2O fluxes were plotted as points and modeled N_2O fluxes were plotted as lines on the same graph. Visual inspection of these graphs showed whether the model could predict general trends and magnitudes of emissions during the measurement period. If the model performs poorly compared to field measurements, further model evaluation is unnecessary and model input and formulation should be investigated instead. Cumulative N_2O emissions during the growing season were obtained through linear interpolation of measurement data and compared to model predictions. These results were plotted as bar graphs and statistical analyses (as described in Section 3.1.3) were used to determine if the model accurately predicts cumulative N_2O emissions. Since N_2O emissions are considered at the annual scale when reporting national greenhouse gas emissions [27], this level of analysis was sufficient for overall performance evaluation but was not useful in identifying sources of potential model issues. Modeled vs. measured N_2O fluxes were plotted as points and compared to a 1:1 line. The closer the points are to the 1:1 line, the more accurate the model appears. In addition, this form of visual inspection can identify possible outliers, systematic shifts, or differences in apparent trends, which are used to recognize significant model formulation issues [64].

Quantitative analysis included root mean square error (RMSE) and coefficient of determination (R^2). RMSE as a percentage was calculated by

$$RMSE(\%) = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^{n}(O_i - P_i)^2}{n}} \tag{4}$$

where O_i is the ith measured value, P_i is the ith modeled value, n is the number of values compared, and $\bar{O}$ is the average measured value.

RMSE was only used to compare cumulative emissions because daily scale flux comparisons under this method typically show poor performance even when the model performs well [53]. This is because it considers whether measurements on specific days are similar, so a model that lags measurements by a day would perform poorly for RMSE even though the predictions are accurate after accounting for the lag [53]. R^2 was calculated in Microsoft Excel (2016) using linear regression to quantify the association between modeled and measured results. A low R^2 value (near 0) indicates that the modeled and measured results do not follow the same trends. While a high R^2 value (near 1) indicates high association, it does not necessarily prove a good model as the relationship may be skewed from observations. For identical reasons to those explained in the previous paragraph, R^2 values were only considered for cumulative emissions.

DNDC includes uncertainty analysis within its user interface and uses a Monte Carlo simulation to determine model uncertainty based on variation in model inputs [65]. The Monte Carlo technique randomly selects values within the input probability distributions and uses these values to obtain model output [64]. Using thousands of Monte Carlo runs, this method develops a distribution of a given model output, which is interpreted as its range of uncertainty [64]. DNDC allows users to enter ranges of uncertainty for various model inputs as percentage deviations from the initial value [65]. DNDC assumes uniform distribution, divides the input ranges into eight equal sections, and randomly selects from the section medians for each parameter to create each new Monte Carlo run [65]. Sensitivity analysis was done by varying more than one input parameter at a time using the Monte Carlo simulation [64]. Under this approach, 4,096 Monte Carlo runs were completed for each comparison. Sensitivity analysis was used to determine the combined effects caused by modifications to select parameters, which informed the chosen model calibration approach, and is described in further detail in Appendix C: Parameter Optimization. Spearman's Rank correlation was used to find the correlation coefficient between given soil parameters and nitrous oxide flux. The correlation coefficient, ranging from -1 to 1, indicates how correlated two parameters are and if the correlation is positive or negative. If the correlation coefficient was near zero, nitrous oxide flux was considered insensitive to that parameter.

3.2.3 Model calibration

Model calibration was completed through parameter optimization of soil parameters (Table 6) to obtain the best model agreement with cumulative N_2O flux measurements [64]. Parameter optimization involves changing the value of each input parameter one-at-a-time within its range of uncertainty and selecting the value that brings model output closest to measurements [64]. Initially four soil parameters (pH, clay content, SOC, and bulk density) were chosen based on a literature review, availability of site-specific initial values, and uncertainty of these input parameters. The number of parameters was reduced to three (pH, clay content, and SOC) in subsequent runs after conducting sensitivity analysis that showed low sensitivity of N_2O fluxes to soil bulk density. Uncertainty ranges (Table 6) were calculated as the range of values found in the vicinity of the field site using the Web Soil Survey [54]. For additional details and R code used in model calibration, see Appendix C: Parameter Optimization.

Table 6. Parameters used in model calibration, their initial values, and ranges tested by parameter optimization

Parameter	Initial value	Range tested
Fort Collins, CO		
pH	7.6	7.2-8.2
clay content (%)	31	21-31
SOC (g kg^{-1})	12.5	7.5-17.5
bulk density (g cm^{-3})	1.39	1.30-1.47
Rosemount, MN		
pH	6.5	6-7
clay content (%)	12.7	8-18
SOC (g kg^{-1})	28	25-35
bulk density (g cm^{-3})	1.45	1.3-1.6

Initially, the model was calibrated for one field management condition and validated across other field managements. Subsequent runs were calibrated for each field management individually based on the first year of field measurements and was validated by subsequent years of field measurements under the same conditions. In all cases, model evaluation (3.2.2) was conducted to assess model improvement. Unless specifically identified as calibration results, all model results are based on the default model.

4. Results

4.1 Measurements

Overall, Illinois field N_2O emissions were generally low (0-211 gN/ha/d) compared to other studies (Table 1), making observed differences between them difficult to discern. N_2O emissions peaked on June 23, 2016, two months after fertilization within fertilized, tilled plots (Figure 8). N_2O emissions from all plots reached levels below detection within three months of fertilization. Unfertilized control plots also experienced a slight peak in N_2O emissions two months after planting when temperature and precipitation were high. On any given field sampling date, fertilized plots had up to 94% higher magnitude N_2O fluxes than unfertilized ones. Differences between cover cropped and plots without cover cropping were less predictable, where cover cropping sometimes increased N_2O flux by as much as 98% and sometimes decreased flux by 232% relative to plots without cover cropping.

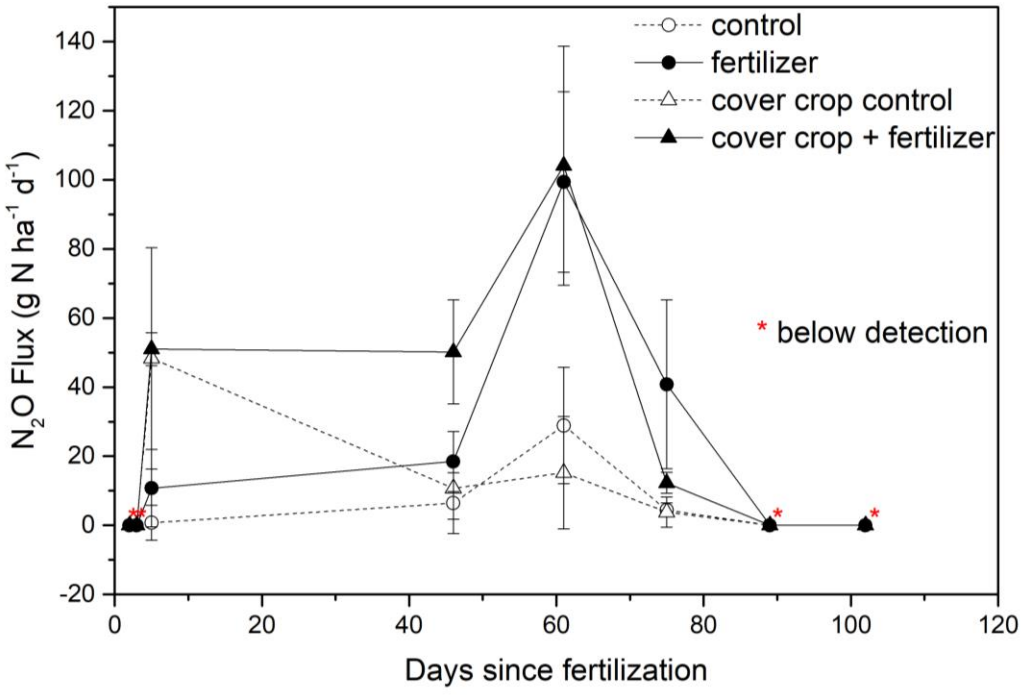

Figure 8. Measured N_2O flux from Illinois tilled plots in 2016 comparing fertilizer and cover crop treatments with time from fertilization. Control plots received no fertilizer. Asterisks indicate fluxes that were below the detection limit of the gas chromatograph (0.1 ppm). Error bars based on standard deviation of three replicate field plots.

In addition, both the cover crop control and fertilized plots exhibited elevated N_2O emissions shortly after planting, although the increase was only significantly different for the field that was fertilized (Figure 9).

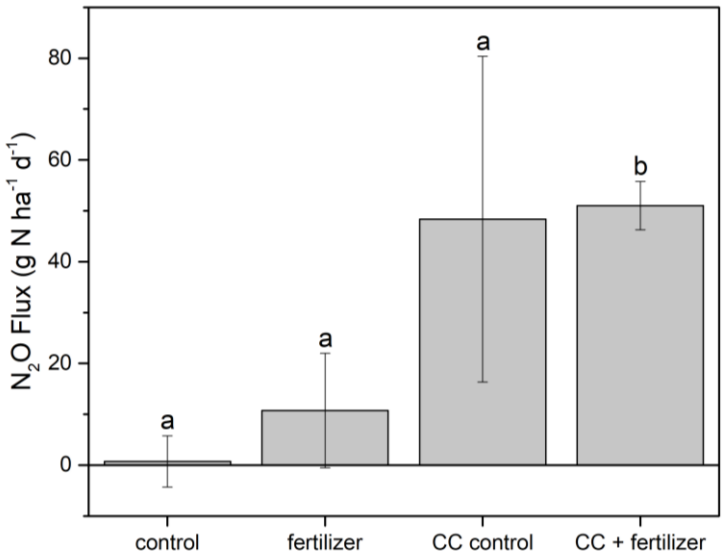

Figure 9. Measured N_2O flux after cover crop termination in Illinois tilled plots. Data from April 28, 2016, the first field sampling date above detection after cover crop was terminated and fertilizer was applied. Error bars based on standard deviation of three field replicates. Letters indicate statistical difference between treatments, where significance was for $P<0.05$; treatments with the same letter are not significantly different. The fertilized plot with cover cropping was significantly different from all other tilled treatments on that sampling date.

Within untilled plots, the N_2O emission peak occurred on June 23, 2016, approximately one month after fertilization (Figure 10). Thus, the N_2O emission peaks occurred on the same date at both sites, regardless of fertilization date. Although N_2O flux between corn rows was higher than in-row emissions, this difference was not significant at 95% confidence. N_2O emissions were below detection two months after fertilization.

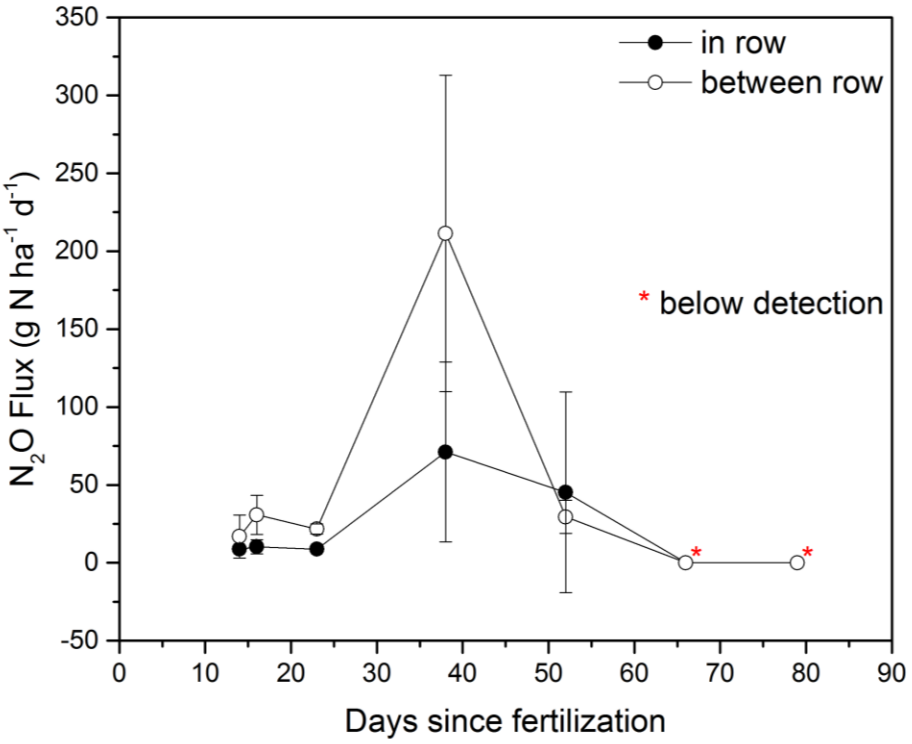

Figure 10. Measured N_2O flux comparing in-row and between-row chambers with time from fertilization in Illinois no till plot in 2016. In-row chambers were placed in line with corn crops, while between-row chambers were in the space between corn rows. Asterisks indicate fluxes that were below the detection limit of the gas chromatograph (0.1 ppm). Error bars based on standard deviation of two or three field replicates, where three replicates were implemented beginning 38 days after fertilization.

Comparing all treatments, fertilized plots showed higher average N_2O emissions than unfertilized plots (Figure 11). However, this difference was only statistically significant ($P<0.05$) between the chisel plow control plot and the chisel plow, cover crop, fertilized plot.

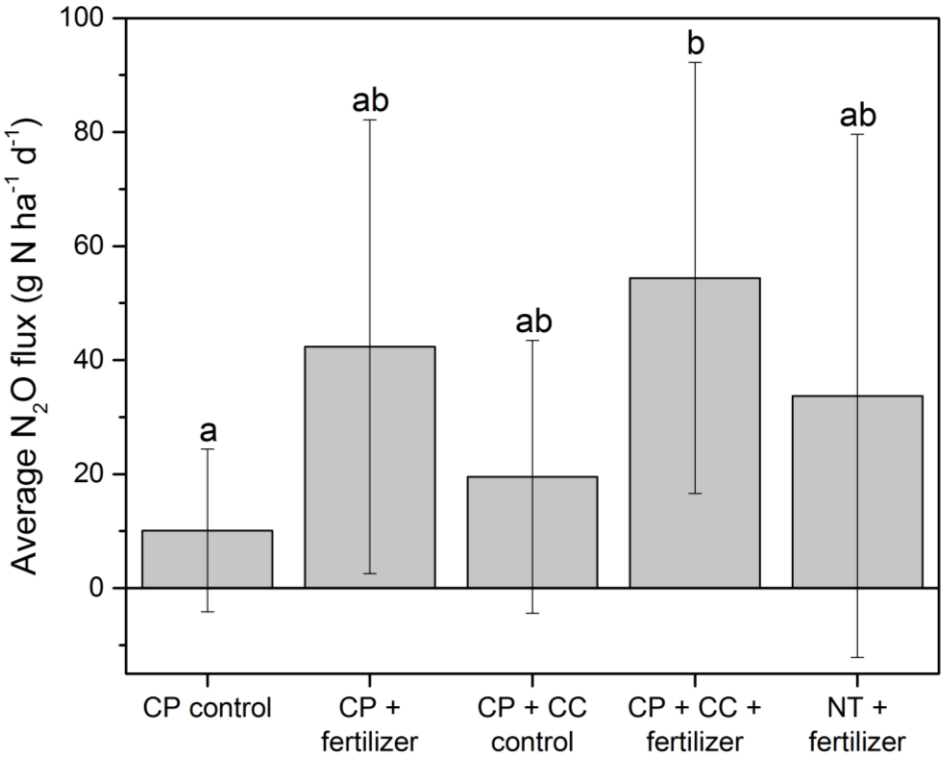

Figure 11. Average N_2O flux for dates above detection in 2016 for Illinois plots comparing tillage (CP-chisel plow, NT-no till), fertilizer (where specified), and cover cropping (CC). Error bars based on standard deviation of three field replicates and four dates. For the Lo Farm (no tillage), only in row chambers were included here, for direct comparison with PZM chamber fluxes. Letters indicate statistical difference between treatments, where significance was for $P<0.05$; treatments with the same letter were not significantly different. Only the chisel plow control and cover crop + fertilizer plots were significantly different.

4.2 Modeling

Modeled N_2O emissions for Illinois were consistent with field measurements (Figure 12-Figure 13). The highest modeled N_2O peaks occurred just before planting and fertilization in fertilized plots, and in February for unfertilized plots. The limited number of field measurements prevented further model evaluation for the Illinois sites.

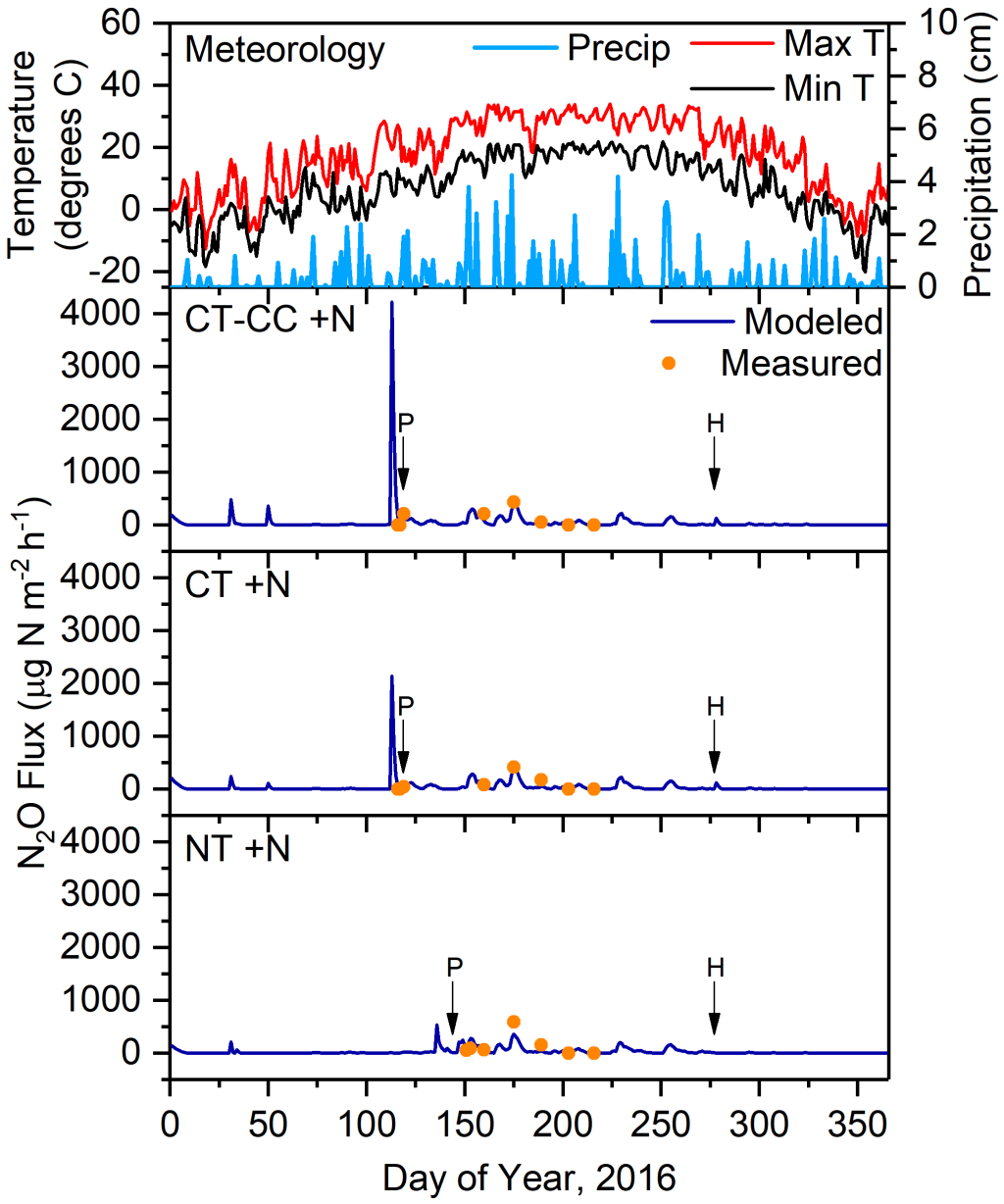

Figure 12. Illinois daily meteorology and comparison of modeled and measured nitrous oxide flux in 2016 for fertilized plots. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, for the treatments considered at the site: conventional tillage (CT), no tillage (NT), and cover crop (CC). Arrows indicate planting (P) and harvest (H). For tilled plots, fertilizer was applied the same day as planting; in the no till plot, fertilization was ten days before planting.

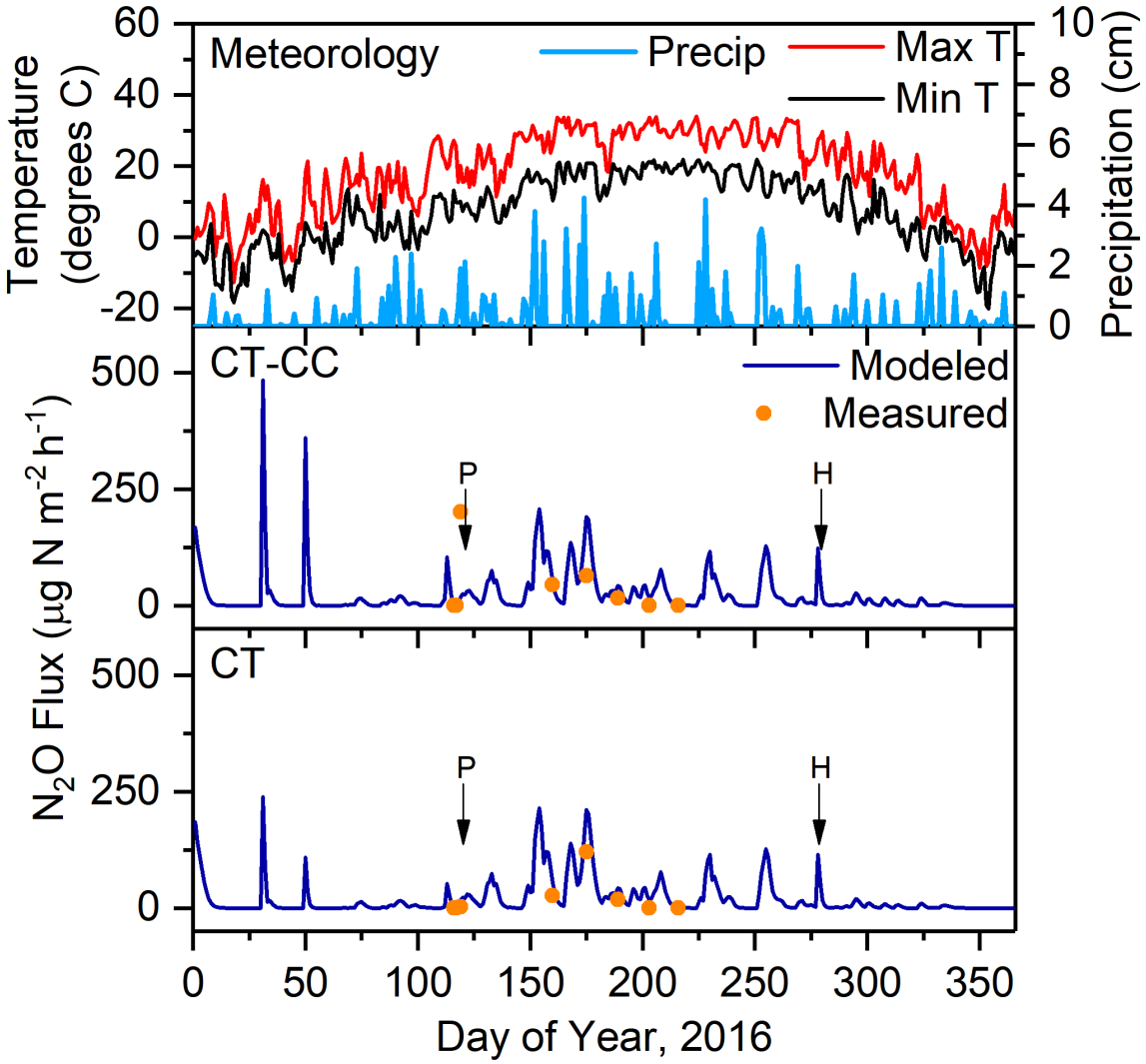

Figure 13. Illinois daily meteorology and comparison of modeled and measured nitrous oxide flux in 2016 for unfertilized plots. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, for the no-fertilizer treatments considered at the site: conventional tillage (CT) and cover crop (CC). Arrows indicate planting (P) and harvest (H).

Model evaluation was conducted using by comparing DNDC predicted N_2O fluxes to field measurement data from Minnesota and Colorado. Minnesota precipitation (Figure 14) was much lower than average in 2008 and 2009, returning to near average levels in 2010. Modeled N_2O emissions often overpredicted, as compared to field measurements (Figure 14), especially in 2010. While modeled N_2O flux peaks in Minnesota occurred shortly after fertilization in 2008 and 2009, the highest peak in 2010 occurred before fertilization. This peak also occurred before field measurements began for the year, preventing direct comparisons during that time. Overall, modeled and measured N_2O emissions at the daily scale were not well matched in Minnesota for all four treatments from 2008-2010. However, when considering the cumulative emissions during the growing season (Figure 15), modeled and measured N_2O fluxes were not significantly different ($P=0.36$). Considering the impact of field management on N_2O flux, fertilizer significantly increased modeled and measured emissions ($P=0.006$ and 0.04, respectively), but tillage showed no significant effect ($P=1$ and 0.34 for modeled and measured, respectively).

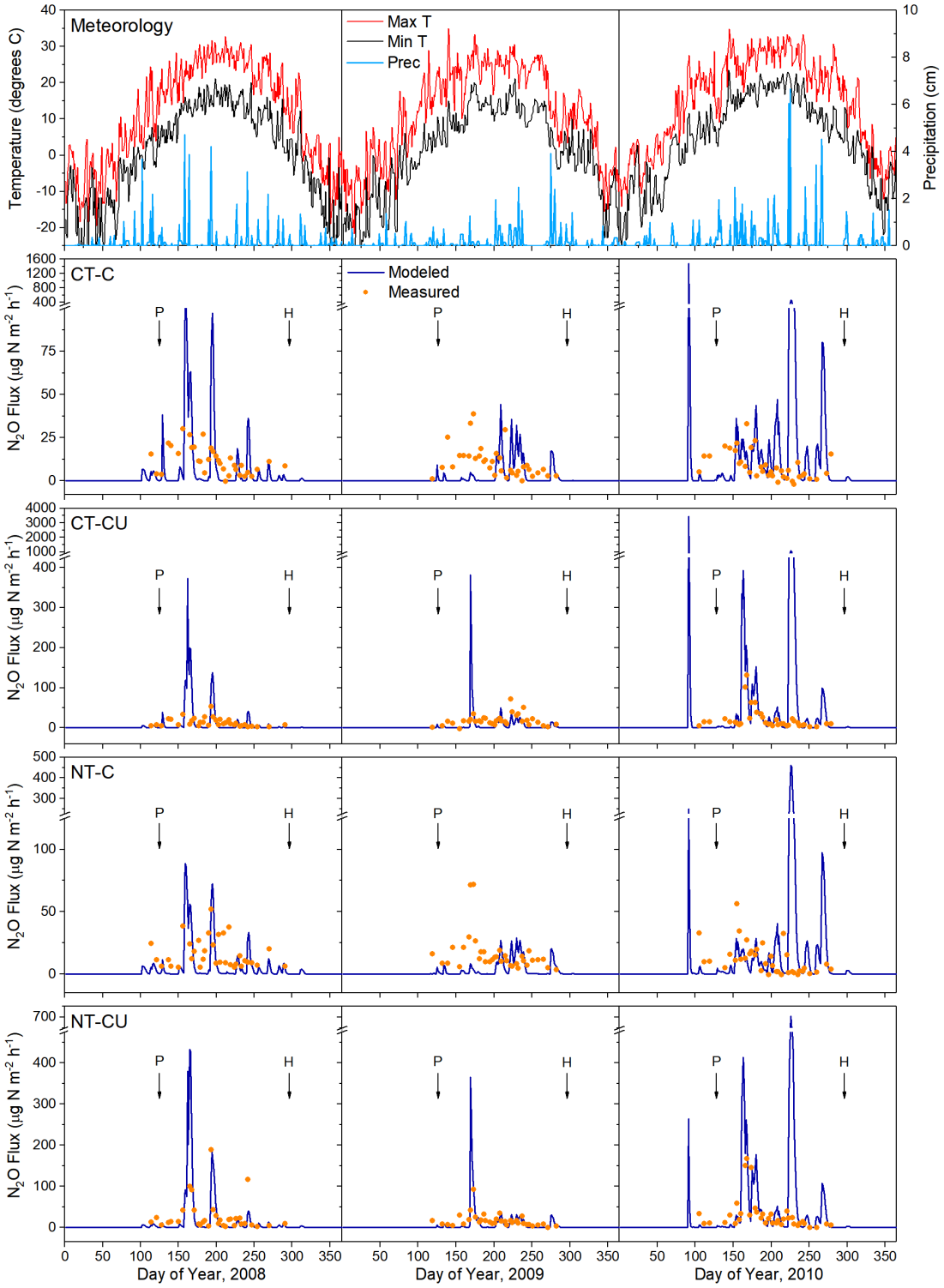

Figure 14. Minnesota daily meteorology and comparison of modeled and measured nitrous oxide flux from 2008-2010. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, for the treatments considered at the site: conventional tillage (CT), no tillage (NT), control urea fertilizer at 4.5 kg N ha^{-1} (C), and conventional urea fertilizer at 146 kg N ha^{-1} (CU). Arrows indicate planting (P) and harvest (H) in each year. Note the different scales on the y-axes.

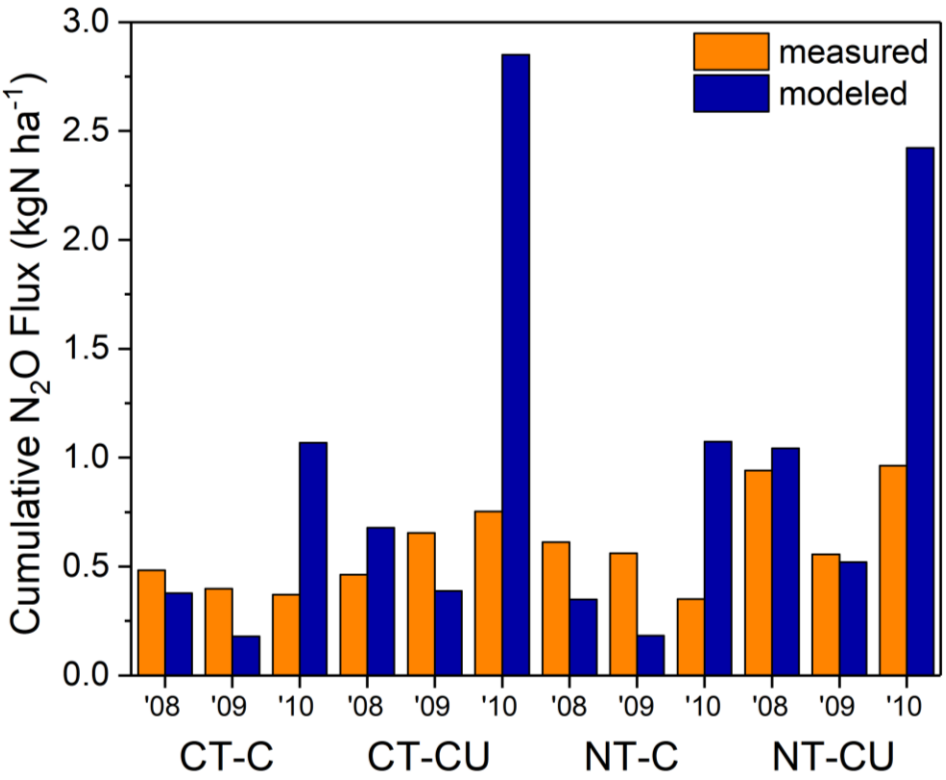

Figure 15. Minnesota cumulative measured and modeled nitrous oxide flux during the growing season for the treatments considered at the site: conventional tillage (CT), no tillage (NT), control urea fertilizer at 4.5 kg N ha^{-1} (C), and conventional urea fertilizer at 146 kg N ha^{-1} (CU).

Similar to Minnesota, Colorado experienced a drought year during the measurement period when precipitation (Figure 16-Figure 18) was below average in 2002 and returned to normal for 2003 and 2004. Modeled N_2O fluxes were more similar to measurements (Figure 16-Figure 18) for 2002 and 2004, but were underestimated in 2003. As in Illinois and Minnesota, model results show high N_2O peaks before fertilization. However, Colorado measurements were year-round, enabling comparisons during this time, and measurements prior to fertilization were low. Daily scale N_2O emissions were not consistently predicted by the model, and cumulative N_2O fluxes during the growing season (Figure 19) were significantly different between modeled and measured ($P=0.0009$). Considering the impact of field management on N_2O flux, fertilizer significantly increased modeled and measured emissions ($P=0.0002$ and 0.0005, respectively). Crop rotation showed no significant effect ($P=0.08$ and 0.79 for modeled and measured, respectively). Similar to Minnesota results, tillage also showed no significant effect in Colorado ($P=0.61$ and 0.53 for modeled and measured, respectively).

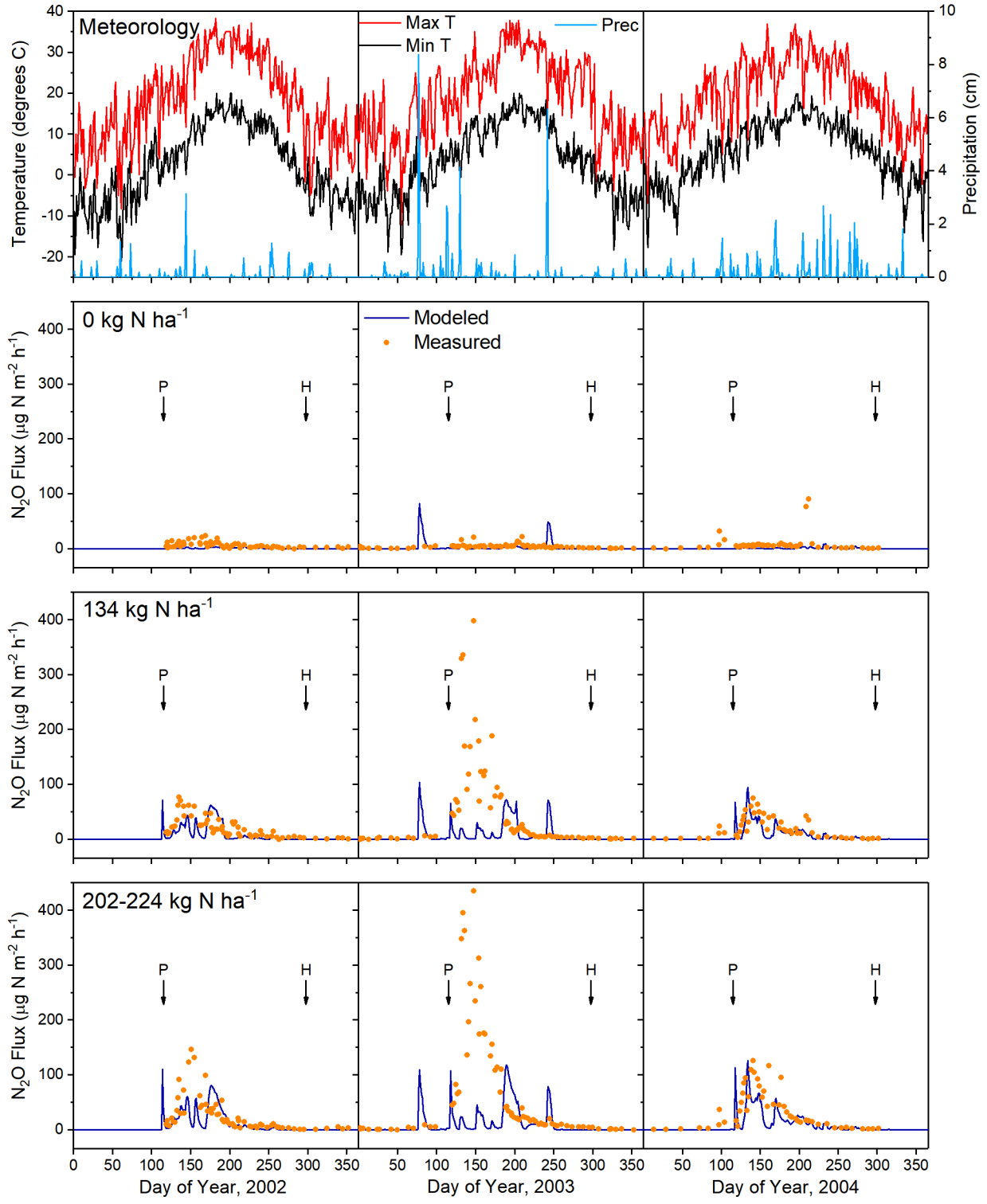

Figure 16. Colorado continuous corn, conventional tillage treatment plot comparison of modeled and measured nitrous oxide flux from 2002-2004 and daily meteorology. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, at the three fertilizer treatment rates in the continuous corn, conventionally tilled plots. Arrows indicate planting (P) and harvest (H) in each year.

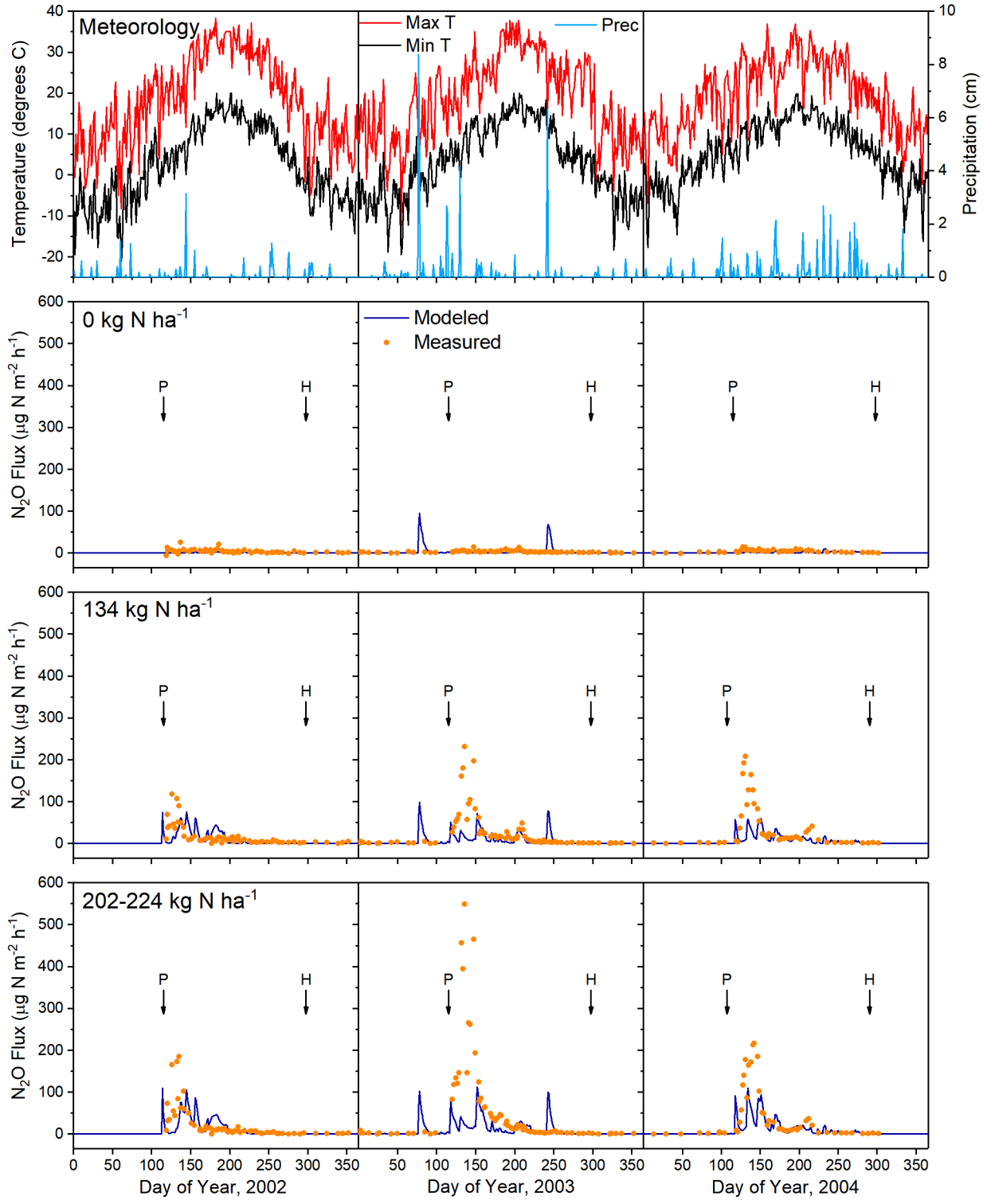

Figure 17. Colorado continuous corn, no tillage treatment plot comparison of modeled and measured nitrous oxide flux from 2002-2004 and daily meteorology. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, at the three fertilizer treatment rates in the continuous corn, no tilled plots. Arrows indicate planting (P) and harvest (H) in each year.

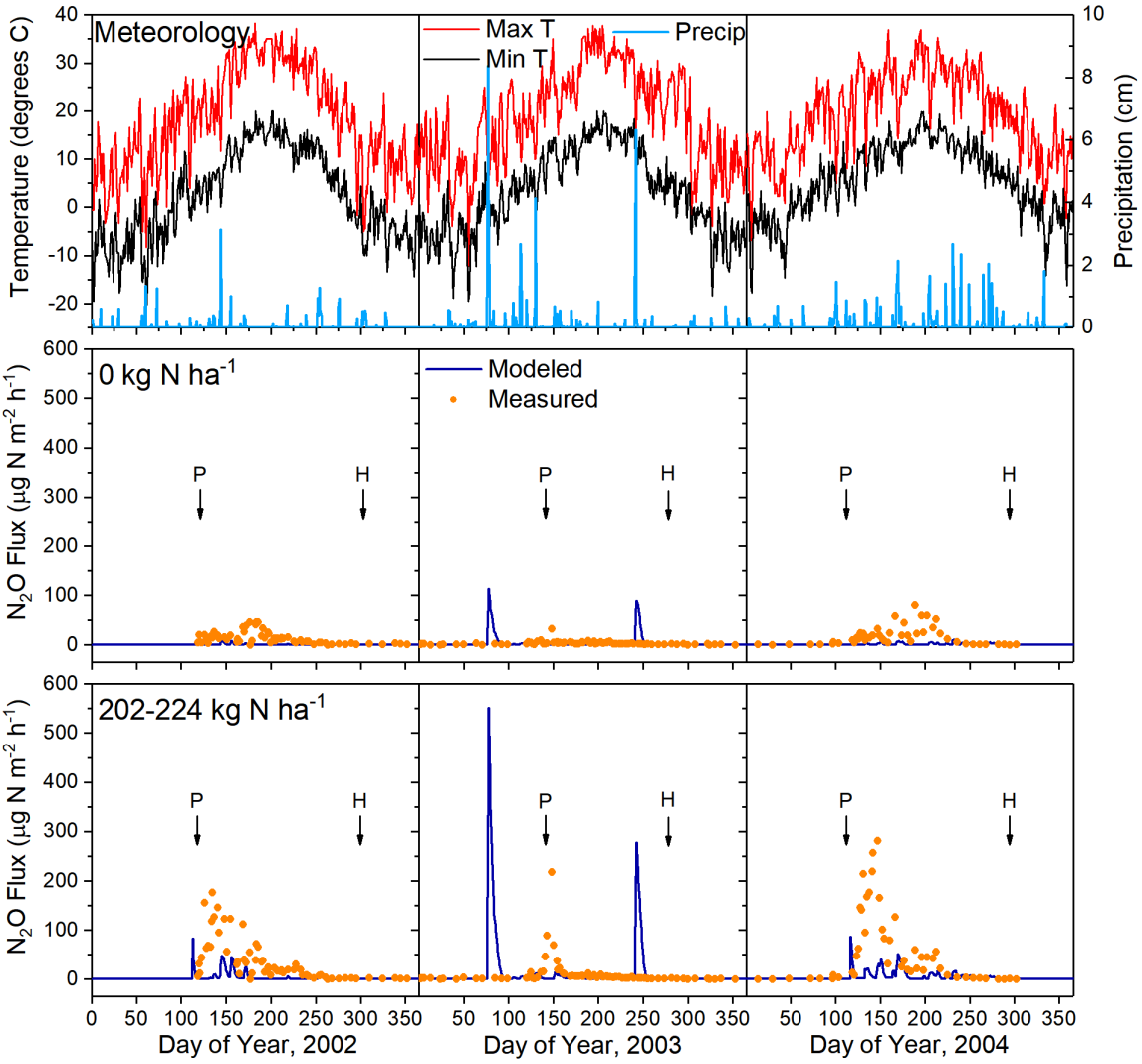

Figure 18. Colorado corn-soybean rotation, no tillage treatment plot comparison of modeled and measured nitrous oxide flux from 2002-2004 and daily meteorology. The top panel shows maximum and minimum temperature in red and black, respectively, and precipitation in light blue. The remaining panels show modeled and measured nitrous oxide as solid blue line and orange points, respectively, at the two fertilizer treatment rates in the corn-soybean rotation, no tilled plots. Arrows indicate planting (P) and harvest (H) in each year.

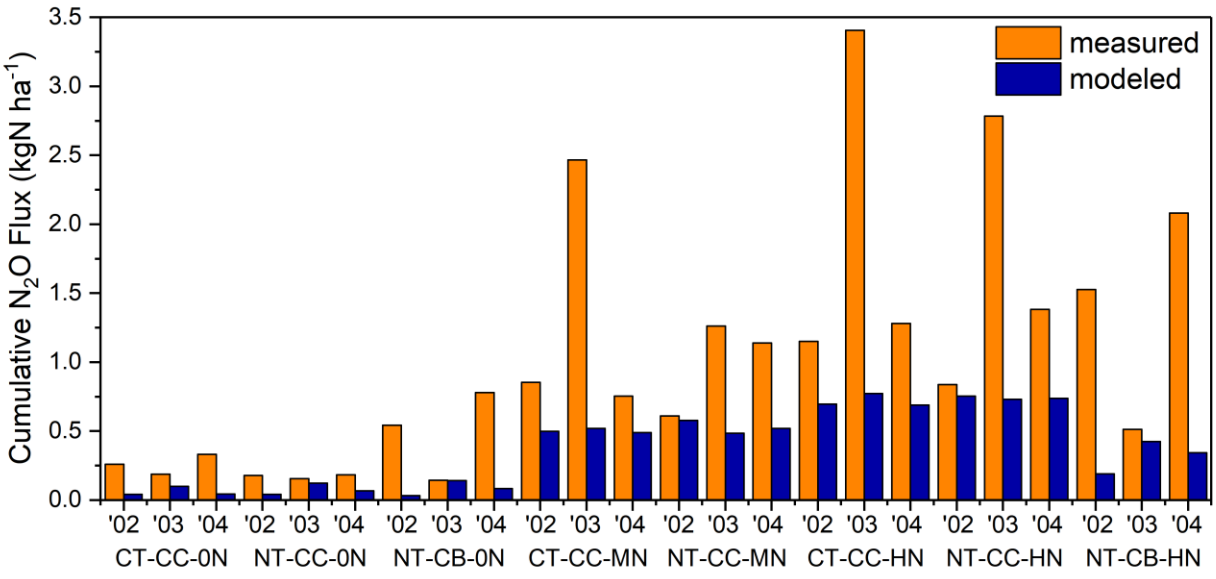

Figure 19. Colorado cumulative measured and modeled nitrous oxide flux during the growing season for the treatments considered at the site: conventional tillage (CT), no tillage (NT), continuous-corn (CC), corn-soybean (CB), no fertilizer (0N), moderate fertilizer at 134 kg N ha-1 (MN), and high fertilizer at 202-224 kg N ha^{-1} (HN).

Modeled vs. measured N_2O flux plots (Figure 20) show that while DNDC predicted N_2O emissions better for Minnesota, the model did not perform well overall. Minnesota's slope was 1.53, while Colorado's was 0.20. The association between modeled and measured results (R^2) was 0.67 and 0.41 for Minnesota and Colorado, respectively.

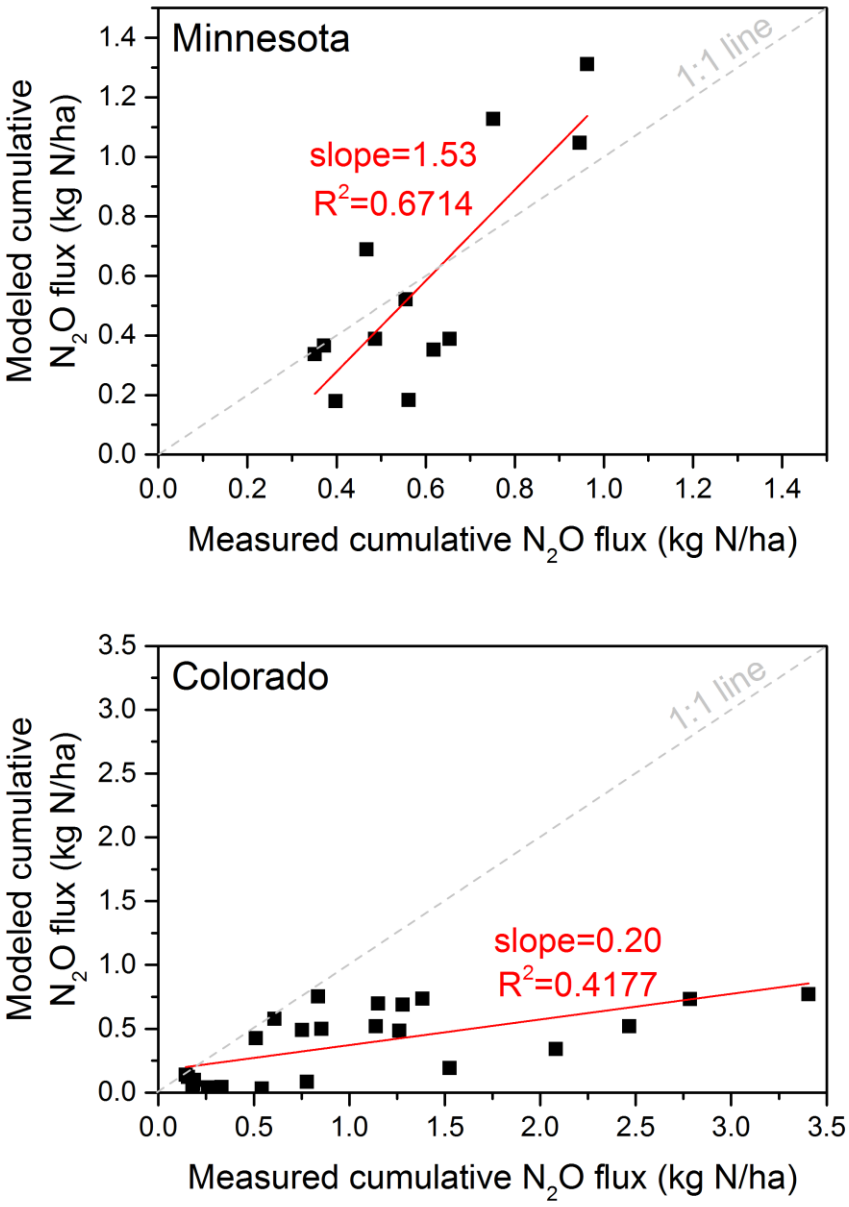

Figure 20. Modeled versus measured cumulative N_2O flux for Minnesota (top) and Colorado (bottom) treatments over three years. Each point represents the cumulative N_2O flux for one treatment and one year at the site. Slope is used to compare to the 1:1 line, where values closer to 1 indicate a more accurate model. Coefficient of determination (R^2) is used to show association between modeled and measured results, where the closer it is to 1, the better the association.

The DNDC model was calibrated by parameter optimization to improve model performance. The default and calibrated model versions were compared to assess model improvement. Comparing modeled vs. measured N_2O flux plots before and after calibration (Figure 21), model calibration only improved slope for Minnesota, and did not improve association for either site. RMSE after calibration (Figure 22) was only decreased by 10% and 6% for Minnesota and Colorado, respectively. Separating the RMSE values by calibration or validation year (Figure 23), calibration decreases RMSE by 92% and 27% for Minnesota and Colorado, respectively. However, the benefits did not carry over. In Minnesota, the RMSE was only decreased by 63% in validation year one and increased by 47% in validation year two. In Colorado, the RMSE was increased by 3% in validation year one and only decreased by 24% in validation year two.

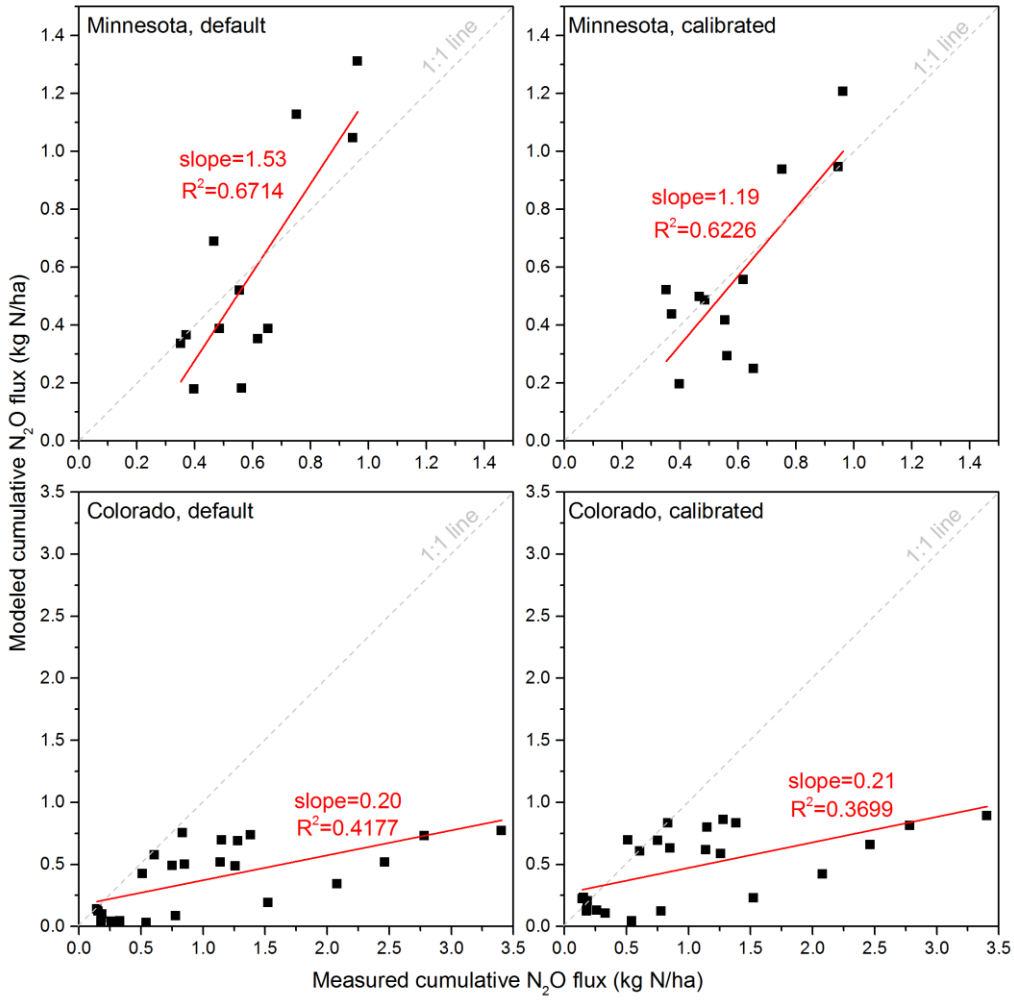

Figure 21. Comparison of modeled versus measured cumulative N_2O flux graphs before and after model calibration for the two sites. Each point represents the cumulative N_2O flux for one treatment and one year at the site.

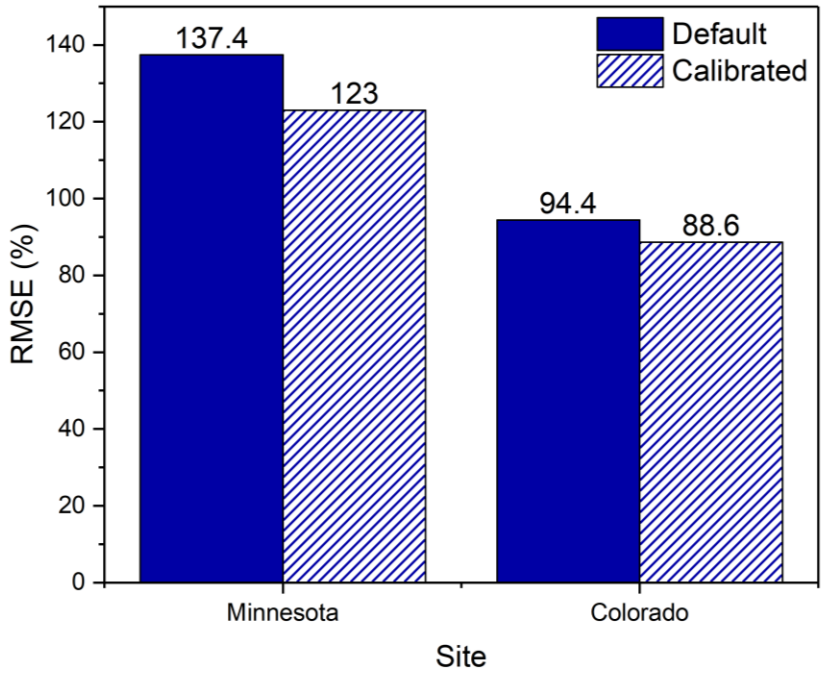

Figure 22. Root mean square error (RMSE) as a percent for modeled cumulative N_2O emissions before and after model calibration. Lower RMSE indicates a more accurate model.

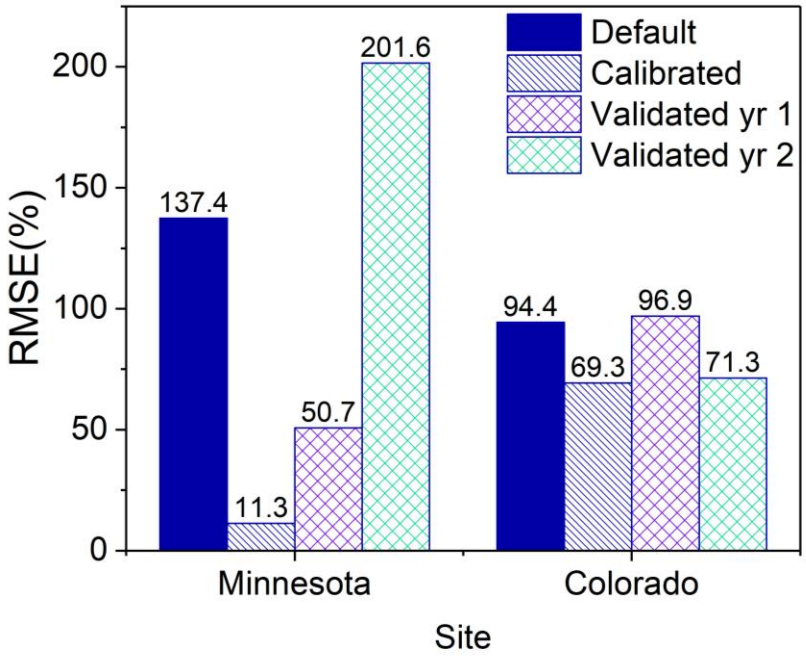

Figure 23. Root mean square error (RMSE) as a percent for modeled cumulative N_2O emissions before and after model calibration and for the two years of validation. Lower RMSE indicates a more accurate model.

5. Discussion and Conclusion

While N-rich fertilizers have helped sustain the increasing human population, they are also damaging the environment [2]. Much of the nitrogen applied to crops is leached to water, lost to the atmosphere, or lost as food and human waste, leading to numerous negative environmental impacts including climate change, smog, acid rain, eutrophication, and loss of biodiversity [2]. Thus, it is imperative to manage the loss of N from agriculture to sustain both our food supply and the environment. To manage N losses, we must first use appropriate methods for quantifying N losses and identify agricultural practices that best mitigate these losses.

This study compared measured N_2O emissions between corn fields under different fertilizer, tillage, and cover cropping management in Illinois, and evaluated the DNDC model for N_2O emission predictions at sites under these different managements in the United States. The study has shown the importance of model evaluation and the lack of consistent model performance even after calibration. Overall, there were three major conclusions that address the study's aims: (1) field managements in Illinois did not significantly influence N_2O emissions, (2) DNDC did not consistently predict N_2O emissions accurately, and (3) model calibration only improved predictions for the year and treatment it was calibrated for. This section discusses the results that led to each conclusion and associated limitations. In addition, this section discusses the influence of precipitation on measured N_2O emissions and model performance, and discusses areas that need further study and model improvement.

Modeled daily N_2O emissions for Illinois were of the same magnitude and trend of the field measurements. However, with the limited number of field measurements, cumulative N_2O emissions could not be accurately calculated for Illinois. Therefore, model evaluation and calibrations were based on the Minnesota and Colorado sites.

Modeled N_2O emissions for Minnesota and Colorado were often overestimated and underestimated, respectively, which is consistent with some studies [37, 46, 48] and conflicts with others [48-50, 52]. Considering all treatments, cumulative modeled and measured N_2O emissions were significantly different in Colorado but not Minnesota. Even though this difference was significant for Colorado, the RMSE was high and association was very low. Minnesota had higher RMSE error, but higher association as well. Overall, the default model did not predict N_2O emissions well for Colorado or Minnesota. This is consistent with other studies that recommend calibration [37, 48-50, 52]. The difference between cumulative modeled and measured N_2O

emissions could also be due to error inherent in calculation of cumulative measured N_2O emissions. Linear interpolation of measured N_2O fluxes can increase error significantly if field sampling days missed N_2O emission peaks or typically coincided with these peaks.

To improve model performance, I calibrated DNDC using parameter optimization. Calibration improved model predictions for the year it was calibrated for, but improvement was not maintained in subsequent years. Specifically, RMSE decreased dramatically in the calibrated year, but only decreased slightly or increased in validation years. Association was not improved by calibration at either site. Overall, calibration did not significantly improve model performance. In addition, calibration was necessary for each treatment rather than at the site level, which would not be very useful in application even if it was successful. The model needs to be improved to the point where either calibration is unnecessary or calibration is only required once at the site level. Since the current study only used one level of parameter optimization, it is possible that model performance may be improved by utilizing a multi-level parameter optimization approach described in the literature [37]. However, multi-level parameter optimization requires accurate, consistent field measurements of other parameters such as water filled pore space and crop yield. With additional levels of parameter optimization, model default values for crop growth parameters, soil conditions, or microbial dynamics can be specified at the site level. Yet, studies that utilize multi-level parameter optimization are not always successful in improving model performance [37, 47]. In addition, parameter optimization has only been successful at improving predictions of cumulative emissions [49, 50, 52], so the model requires further improvement at the daily scale.

Field N_2O emissions in Champaign, Illinois, were low for all plots. Overall, field management at the Illinois sites did not have a significant effect on field N_2O emissions. This finding is consistent with conclusions of other studies considering the influence of tillage [16, 23, 25, 39] and cover cropping [20, 23]. However, other studies comparing fertilizer rates found that fertilizer application rate significantly influenced N_2O emissions [17, 19, 20, 23, 28, 29, 35]. Any differences in N_2O emissions between managements for this site may have been obscured by the fact that emissions were generally low.

For the Minnesota and Colorado field studies, fertilizer was the only factor that significantly influenced both modeled and measured N_2O flux. Similar to the Illinois site, tillage did not significantly influence N_2O emissions in Minnesota or Colorado. This model result agrees with the measurements, as the chosen studies both found tillage to be insignificant. In addition, a

previous modeling study also observed that DNDC was able to capture differences between fertilized and unfertilized plots but no other managements [47]. It is likely that the difference is only significant for fertilizer in these cases because fertilizer impact is the best understood, as compared to the influence of tillage or cover cropping, which are conflicting in the literature or not commonly studied. Conflicting outcomes of these management makes it difficult to parameterize the model. Also, without the interaction effects associated with these managements, model equations and relationships may be poorly defined. It is recommended to model N_2O emissions for sites that found tillage and other factors significant to see if the model is able to replicate these findings. Currently, the model was capable of finding significance in all the same factors identified as important through field studies.

Field N_2O emissions in Illinois were highest within two months of fertilization and were below detection after three months. This trend is consistent with observations from other field studies in the United States [15-17, 19, 21]. The highest modeled N_2O emission peaks occurred during time periods without field measurements for comparison. Without more data, it cannot be discerned if these model peaks are accurate or inaccurate. Therefore, future work will include year-round field sampling to determine if these pre-planting and fertilization peaks exist.

Similar to Illinois, modeled N_2O flux peaks occurred before fertilization in Minnesota. Without field measurements during that time, this peak could not be compared. Fortunately, Colorado's year-round measurements allowed for a direct comparison before fertilization. Colorado N_2O measurements prior to fertilization were low, suggesting that the pre-fertilization N_2O peaks in the model are inaccurate. Another modeling study also found high N_2O fluxes prior to fertilization, which they attributed to the model's overprediction of water filled pore space, an important parameter in the calculation of N_2O emissions [46]. It is important to compare modeled and measured N_2O fluxes before fertilization for additional sites to determine if low emissions are uniform everywhere. Thus, it is recommended for more studies to include year-round field gas sampling, and for modeling studies to include predictions for the entire year rather than just the growing season.

For the Illinois fields, N_2O emission peaks occurred on the same date at both field sites, regardless of fertilization dates, which occurred 23 days apart. This shows that weather and climate may influence emissions more than fertilizer timing. In general, N_2O emission peaks often corresponded with higher precipitation and temperature. This is likely due to precipitation

increasing soil water content, leading to more anaerobic zones and higher denitrification rates. In addition, denitrification rates increase exponentially with increasing temperature [41]. The Minnesota field study identified a relationship between precipitation and field N_2O emissions [16], which supports the observations of my study. The years where the model had the worst predictions were years of high precipitation following at least one year of drought. However, DNDC did not consistently predict the influence of the precipitation on emissions. Therefore, it is important to further understand the influence precipitation has on N_2O emissions, improving the role of precipitation in model processes.

In conclusion, the DNDC model only appeared to consistently perform well for the Illinois site, while Minnesota and Colorado's modeled N_2O emissions were often overestimated or underestimated. In addition, model calibration by parameter optimization did not improve model performance beyond the treatment and year for which it was calibrated. Field N_2O emissions were generally low in Illinois, and overall, field managements did not significantly influence emissions. For the Minnesota and Colorado sites, DNDC was capable of detecting the same significant factors influencing N_2O emissions that were identified by the field studies. N_2O emissions peaks occurred after fertilization in the field studies and prior to fertilization in the model, and both N_2O emission peaks and model performance were influenced by precipitation.

Overall, this study shows that DNDC model performance varies with location and time, indicating that climate and weather patterns strongly influence model outcomes. Therefore, it is recommended that additional year-round field N_2O measurement campaigns are compared to model predictions to identify model inconsistencies. In addition, efforts need to be aimed at improving our understanding of precipitation's influence on field emissions.

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7. Appendices

Appendix A: Chamber Construction

The following materials and methods were adapted from those published by Parkin and Venterea [7]. While the basic procedure remains identical, these materials and methods are more detailed. Materials include specific manufacturers and part numbers for items used in the construction of 17 chamber tops and 28 chamber bases. Also included are the specific tools used in these methods. Parkin and Venterea provide visual instructions (photographs) which are not reproduced here [7].

Materials

PVC pipe, 12” diameter, schedule 40 (locally sourced)

Straight union fittings, ¼” PP (Cole-Parmer, cat. # EW-30802-94)

Tractor tire tube, 15.5R38 (Pete’s Tire Store, cat. # 556998)

PVC sheet, grey, ¼” thick, grade 1 type 1, .25”x24”x48” (US Plastic, cat. # 45088)

Metalized Mylar Film tape, 2” width, silver (CS Hyde Company, cat. # 24-MF-SLV-2)

PVC purple primer and cement (Home Depot, cat. # 462620)

Rubber weatherseal, 3/8” wide x ¼” thick, “D” profile (Home Depot, cat. # 518441)

Stainless steel tubing, ¼” (Grainger, cat. # 3ACH4)

20 mm butyl rubber stoppers (Sigma-Aldrich, cat. # 27232)

Duct tape

Scissors

Jigsaw

Drill w/ ½” bit and bit slightly smaller than tap

Power saw

Engine Lathe

Clamps

Tap

Permanent marker

Ruler

Procedure

1. From the PVC pipe, cut 10 cm long sections for chamber tops and 15 cm long sections for chamber bases. Make a 45 degree bevel on one edge of the chamber bases. This step was outsourced to a machine shop that used a power saw for cutting sections and an Engine Lathe for beveling edges.
2. From the stainless steel tubing, cut 15 cm long sections for vents. Attach each piece of SS tubing to a fitting. The opposite end of the fitting can be unscrewed and the cap can be discarded.
3. Trace the chamber top onto the PVC sheets and cut out the circles using a jigsaw. To prevent melting and jamming, run the jigsaw on a slower setting and take periodic breaks to remove plastic shavings.
4. Clean the outside edge of each circle and the top edge of each chamber top. Apply PVC primer to the cleaned areas and allow to dry. Next, apply PVC cement to the same areas and quickly attach the PVC circle to the top edge of the chamber top. Hold the pieces together for a few minutes before placing the clamps. Allow the pieces to remain clamped for at least 24 hours.
5. Using the drill, drill a ½" hole in the PVC circle halfway between the center and outside edge. On the same chamber top, drill a hole slightly smaller than tap about 1" from the top edge of the PVC pipe. The two holes should be offset from each other (approximately 90 degrees). Using the tap, thread the hole. Turn the tap 4-5 times at first and then attempt to screw-in the fitting from the inside edge. Continue this process, alternating between cranking the tap and trying the fitting, until the fitting screws into the hole snuggly. Ensure the hole is kept as small as possible to provide the most air-tight seal.
6. Cut 7 cm wide strips of the tire tube to make rings for sealing the chamber top and bottom. Cut each strip from the outside diameter to inside diameter of the tire tube. Snuggly attach one strip to the bottom edge of each chamber top with half hanging off the bottom. Using duct tape, tape the strips in place on the outside edge of the chamber tops.
7. Cover the entire outside of each chamber top with the reflective Mylar tape. Poke holes in the top and side where the drilled holes are located.
8. Fold back the tire tubes and flip the chamber tops upside down. Cut sections of weatherseal the length of the circumference of the chamber top. Peel off the back and press the sticky-

side down along the exposed bottom edge of each chamber top. Stack chambers or use other heavy objects to hold the weather seal in place when not in use.

9. Place a butyl rubber stopper in each chamber top.

Appendix B: N_2O Sampling Protocol

These sampling protocols were developed based on literature recommendations [6, 7, 57]. Base installation method (part A, step 5) was modified because the field soil was too compact to insert bases easily. For most the 2016 field sampling campaign, sampling time points of 0, 20, 40, and 60 minutes were used because initial measurements at shorter time intervals were below detection.

Figure 24. The field sampling kit (left) contains empty sample vials (top up), filled sample vials (top down), syringe, needle, pencil, datasheet, clipboard, and timer. The chamber top (right) is attached to a chamber base installed in a recently tilled and planted corn field in Champaign, IL.

Materials

Assembled chamber top and base (see Appendix A for detailed materials and construction methods)

Clipboard, 6x9” (Amazon, cat. # B00X8I60XM)

Datasheets, 5x8” blank index cards (Amazon, cat. # B002OB49KU)

10 mL clear glass vials (Fisher Scientific, Hampton, NH)

20 mm Pharma-fix PTFE gray butyl rubber septa (SUN SRi, cat. # 405063)

20 mm standard aluminum seals (SUN SRi, cat. # 500334)

20 mL disposable syringe (Fisher Scientific, cat. #22-124-967)

23 gauge needle (Fisher Scientific, cat. # 14-826A)

Standard crimper, 20mm, for aluminum seals (Kebby, cat # 2001-00-C-1A)

Hand shovel

Pry bar, 12 ¾" long, 1 ¾" width

Plank of wood

Vacuum pump

Ruler, 6" (Amazon, cat. # B018NVBM8Q)

Timer (Fisher, cat. # S94843)

Vial carry case, holds 48 vials (Amazon, cat. # B018QBJ58C)

Plastic container

Pencil/pen

Gas bags

A. Installation of Bases (Completed at least 24 hours prior to first sampling time)
    1. First installation: Choose chamber location and obtain GPS coordinates.
    2. Remove any plants, twigs, rocks, etc. that are in the way before placing chamber base (not connected to chamber top) at the appropriate chamber location.
    3. Place the chamber evenly on the ground and place wood plank overtop it.
    4. Step onto wood plank and apply even pressure to insert chamber base into soil until 5 cm of the chamber base is above the soil.
    5. Alternatively to step 3-4 if soil is too hard/compact, dig a ring 10 cm deep, insert chamber, and fill with soil.
    6. Record height inside the chamber base from the ground to the top of the rim at four points: 0°, 90°, 180°, and 270°.

B. Sample Vial Preparation (completed 1-48 hours prior to sampling)
    1. Recap sample vials with new septa and seal using the crimper.
    2. Reuse previously unused sample or backup vials as backup vials. You will need one backup vial for each chamber you plan to sample.
    3. Evacuate sample vials and backup vials for at least 90 seconds each using a vacuum pump at 26.5 in Hg pressure.
    4. Label sample vials.

5. Place sample vials (top up) in proposed sampling order inside carrying case. Place backup vials in any remaining spaces in the carrying case.

C. Gas Sampling Preparation (completed just before sampling)
   1. Place one chamber top with tire tube connector flipped up and septa inserted in sampling port near each chamber base.
   2. Prepare sampling kit (labeled vials, syringe, three needles, clipboard, pencil, ruler). This will be carried with you from chamber to chamber.
   3. Prepare data sheet and place on clipboard.
   4. Ensure backup evacuated vials, syringes, needles, and septa are in the backup materials container. Backup materials container should be accessible, but doesn't need to be carried between chambers.
   5. Assemble syringe by carefully clicking needle into Leur-Lok syringe tip.

D. Gas Sampling
   1. Measure and record height inside the chamber base from the ground to the top of the rim at four points: 0°, 90°, 180°, and 270°.
   2. Start stopwatch. Immediately place chamber top on chamber base #*X* with vent facing downwind. Connect chamber base and top by flipping tire tube connector down over the base.
   3. Take 15 mL gas sample from just beside the chamber (outside) at the same height as the sampling port.
   4. Inject sample into vial C*X*—t_0 using the evacuation test method. The first test is to insert the needle into the vial and observe if the sample automatically begins injecting into the vial. The second test is to push 10 mL of the gas sample into the vial and observe if the sample does not push back into the syringe. If the vial passes both tests (automatically injects, does not push back at 5 mL mark), place vial top down in its location in the carrying case to indicate it is filled with sample. (Optional) If any vials fail one of the two tests, you may attempt a resample *once* using a backup vial. If the backup succeeds, transfer the label from the sample vial to the backup and place the backup vial containing sample top down

in the location where the sample vial would go. Place the failed sample vial top down where the backup vial was taken from. Note the use of a backup on your data sheet under "notes."

5. Flush syringe with air twice.
6. Move to next chamber and repeat #1-5. Continue until all chambers are sampled for t_0.
7. Return to chamber #1.
8. When stopwatch is almost to [time t_1], insert syringe into chamber septa.
9. At [time t_1] remove 15 mL gas sample.
10. Inject sample into vial C*X*—t_1 using the evacuation test method described in #4.
11. Flush syringe with air twice.
12. Move to next chamber and repeat #8-11. Continue until all chambers are sampled for t_1.
13. Repeat #8-12 for the subsequent time t_2 and t_3 until all chambers are sampled.
14. Remove and collect all chamber tops and materials. Leave chamber bases in field unless otherwise specified.

E. Gas Chromatography

1. Fill 1-2 gas bags with Helium from gas tank.
2. Evacuate approximately 20 vials for standards and backups.
3. Prepare two sets of standards (Table 7) using the evacuation test method described in part D step 4. Redo any standards if the vial fails either evacuation test. When preparing samples always inject Helium gas first and N_2O second to preserve N_2O in the case of vial failure.

Table 7. Standards used for GC runs

Name	**Mixture**
Air1	15 mL ambient air
He1	15 mL Helium (He)
Std1	15 mL He + 0.015 mL N_2O
Std2	15 mL He + 0.10 mL N_2O
Std3	15 mL He + 0.15 mL N_2O
Std4	15 mL He + 0.25 mL N_2O
Std5	15 mL He + 0.50 mL N_2O
Std6	15 mL He + 1.0 mL N_2O

4. Fill gas chromatograph trays with one set of standards followed by half of the samples. Fill another set of standards and the remainder of samples. Add the vial separators and place the trays on the GC.

5. Create a new folder for the new GC run. Add a batch file (.gcb) and method file (.gcm) to the folder. Rename the batch file based on the current GC run.
6. Open GC Solution and edit the batch file within post run. Save the batch file.
7. Open GC real time analysis, check the batch file, and press “Start.” The GC runs for approximately 9 minutes per sample.

Appendix C: Parameter Optimization

These model calibration methods were developed based on parameter optimization, as described in 3.2.3, and methods detailed in the literature [37, 49].

A. Choose parameters to optimize

Based on field measurement data available, there are many options available for choosing parameters to optimize. Measurements of water filled pore space can be used to calibrate soil hydrology parameters including field capacity, wilting point, and hydro-conductivity. Field yield data can be used to calibrate crop properties in DNDC. N_2O flux measurements can be used to calibrate soil parameters, microbial activity, and other factors influencing N_2O emissions.

For this study, daily N_2O flux measured periodically throughout the year was the only data readily available for use in model calibration. Thus, parameters were adjusted to better match DNDC predicted N_2O fluxes with field measured N_2O fluxes. Soil parameters were selected for parameter optimization because their initial input values and uncertainty ranges could be obtained from the literature or Web Soil Survey. As described in 3.2.3, four initial soil parameters were chosen: pH, clay content, SOC, and bulk density.

B. Sensitivity analysis

Monte Carlo build into DNDC was run for the sites (3.2.2), varying the four soil parameters mentioned above within their ranges of uncertainty obtained from the Web Soil Survey (Table 6). Spearman's Rank correlation was then used to find the correlation coefficient between given soil parameters and N_2O flux based on Monte Carlo output. Spearman's Rank correlation was selected because it can be used when varying multiple parameters at once.

Correlation coefficients for bulk density were extremely low (<0.01) and were two orders of magnitude smaller than correlation coefficients for pH, clay content, and SOC. Therefore, bulk density was eliminated from the list of parameters to optimize in model calibration to simplify the process.

C. Parameter optimization

DNDC does not have built in parameter optimization or model calibration. Therefore, a combined approach was developed using DNDC and R. Soil parameters were systematically adjusted within their range of uncertainty, and output were compiled by R. Then output was assessed to determine optimized values for each parameter.

Soil parameters were first adjusted in two different orders: (1) pH, clay content, SOC, and (2) SOC, clay content, pH. However, it was determined that order was not important as the final modeled cumulative N_2O flux was independent of order. Therefore, the first order was used for the remainder of calibrations.

The process went as follows:

1. Use linear interpolation between field measured N_2O fluxes and sum total emissions during the growing season (defined as time from planting to harvest).
2. Run default model and calculate cumulative N_2O emissions during the growing season.
3. Choose soil parameter input ranges to test and divide into at least ten steps of equal increment. For example, testing pH from 7.2-8.2, steps of 0.1 could be used: 7.2, 7.3, 7.4, and so on.
4. Manually adjust the value of the first parameter (pH) to the first value in the range (7.2 in the example above).
5. Run the model.
6. Run the R file.

```
setwd("C:/DNDC/Result/Record/Site") # Sets working directory for DNDC output folder
soilN = read.csv("Day_SoilBalanceN_11.csv", head=FALSE, sep=",", skip=5)
# Reads the DNDC output file. Change file name based on year of interest. In this example, the 11th year was of interest.
cgs.N2O = sum(soilN[114:299,16]) # Calculates cumulative N2O emissions for the growing season. Change range for rows based on days of planting and harvest.
setwd("C:/….") # Sets working directory for R output. Insert file directory to access calibration.csv file that is accessible in that location. The file should have two columns, one labeled number and the second N2O. The first will be a running count of model runs, while the second is the cumulative flux calculated by R.
calibration = read.csv("calibration.csv", head=TRUE, sep=",")
N2O = calibration[,2]
N2O = append(N2O, cgs.N2O, after=length(N2O))
write.csv(N2O, file="calibration.csv")
# These steps open the .csv file and add in the latest DNDC run's calculated cumulative emissions to the file.
```

7. Repeat steps 4-6 as the value of the parameter is adjusted systematically by the chosen step (0.1 in the example above).
8. After all steps are run, open the calibration.csv file and copy the cumulative emissions over to a new spreadsheet. Clear out the current data in the .csv file and save so it can be used again in further calibration.
9. Identify the parameter value that produced cumulative emissions closest to those calculated based on measurements in step 1.
10. Adjust the original DNDC input file to the optimized value for the first parameter.
11. Repeat steps 4-9 for each additional soil parameter to identify the optimized value for each.
12. Run the DNDC model using the optimized parameter values as the “calibrated” model version.